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THE STRUCTURE OF CRYSTALS

Supplement for 1930-1934 to the
SECOND EDITION

BY

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Preface

This supplement is a summary of new X-ray structure determinations published during the past four years. As such it follows strictly the form used in Part II of the second edition of "The Structure of Crystals" and aims to include all new studies that lead at least to cell dimensions. In order to facilitate comparison, the figure numbers and paragraph designations are continuations of those in the book. As before, reference numbers, with the year in bold-face, apply to the appended bibliography. The grouping of compounds is identical with that previously used except that in the chapter covering the type RX_3 a separate table has been created for crystals of the composition $R_x(MX_2)_y$.

The writer is indebted to R. B. Corey and K. Pestrecov for much help in making the illustrations and to A. A. Murtland for assistance in preparing the bibliography.

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February, 1935

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Chapter XA. Structures of the Elements

Most of the new data of Table I are accurate determinations of the cell dimensions of the metallic elements. For some metals which can easily be prepared in a state of great chemical purity the edge lengths of the units are now known with an accuracy of 0.0002 to 0.0003 Å. The error for most elements is, however, about ten times greater. Spacings to the fourth decimal place have real significance only if the purity is precisely known, if the sample is sufficiently outgassed and otherwise prepared for measurement and if the temperature is determined. It is not always possible to be sure from the published data that all these conditions have been properly met; the accuracy limits stated in Table I are therefore for the most part those set by the investigators themselves.

New information about the atomic arrangements in elements are recorded in the paragraphs that follow.

(v) In place of the previously described tetragonal structure for gallium there has recently been given an orthorhombic (pseudo-tetragonal) arrangement based on V_h^{18} and having its eight atoms in the special positions:

$$(f) \frac{1}{4}uv; \frac{3}{4}, u, \frac{1}{2}-v; \frac{3}{4}, u+\frac{1}{2}, v; \frac{1}{4}, u+\frac{1}{2}, \frac{1}{2}-v;$$

$$\frac{1}{4}\bar{u}\bar{v}; \frac{3}{4}, \bar{u}, v+\frac{1}{2}; \frac{3}{4}, \frac{1}{2}-u, \bar{v}; \frac{1}{4}, \frac{1}{2}-u, v+\frac{1}{2}$$

with $u=0.159$, $v=0.080$. As is evident from Figure 275 (drawn for comparison with Figure 168) this arrangement is very different from the earlier one.

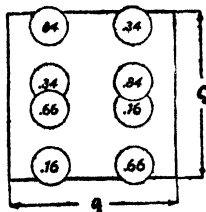
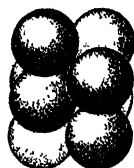


FIG. 275a.—(left) The unit cell of the new orthorhombic arrangement found for metallic gallium as projected on its b-face.

FIG. 275b.—(right) A packing drawing of the gallium atoms shown in a.



(w) The rhombohedral structure of **mercury** has recently been confirmed by single crystal measurements at -50° C. At the same time it is shown that the diffraction data upon which a false hexagonal arrangement was based (1922, 1) apparently were a mixture of the lines of mercury and of solid CO_2 .

(x) Three recent determinations agree with the original in giving **indium** a face-centered tetragonal arrangement with atoms at 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

(y) The X-ray patterns from the β -form of **nitrogen** are thought to indicate that it is a close-packed assemblage of spherical (rotating) N_2 molecules. The parameter chosen for the center of gravity of these molecules is 0.22.

(z) Hexagonal **nickel** prepared by a glow discharge in N_2 has the dimensions stated in the table; prepared in H_2 its unit is larger: $a_0=2.66$ A, $c_0=4.29$ A. It reverts to cubic nickel if heated to 300° C.

(aa) This modification of **tungsten**, said to be obtained by electrolyses under various conditions, is thought to have 8 atoms in its unit. The atoms have been placed at (2a) and (6g) (of 1930, 352) though no intensity data are given in support of this assignment.

(ab) The recorded unit cube of α -**rhodium** is considered to contain 48 atoms. This modification is produced by the reduction of rhodium salts. mixed with the usual form it is also said to result from electrolytic reduction;

(ac) Plastic **sulfur** is rubber-like in that it crystallizes on stretching. The monoclinic unit recorded in the table contains 112 atoms; its space group is given as C_{2h}^2 . As monoclinic sulfur (either stretched or not) ages, the diffraction lines of the orthorhombic form gradually appear.

(ad) The monoclinic cell of α -**Se** contains 32 atoms; its space group is reported to be C_{2h}^2 . Crystals of a solid solution of selenium and sulfur (55.2 wt. % Se), which presumably are isomorphous with a second modification of monoclinic Se, have been assigned a unit different from that of the β -Se reported in the table. The unit of this mixed crystal has $a_0=8.48$ A, $b_0=13.34$ A, $c_0=8.33$ A, $\beta=67^{\circ}30'$.

(ae) The two **uranium** atoms in the centered unit having the dimensions of the table are said to be at 000; $0\frac{1}{2}\frac{1}{2}$. Another determination has made uranium body-centered cubic with $a_0=3.43$ A (1930, 424).

(af) A second form of **beryllium** is reported to be present to the extent of about 10% in samples which have been heated for some time in vacuo at 600° – 800° C. It is described as hexagonal with $a_0=7.1$ A, $c_0=10.8$ A and with ca 60 atoms in this unit cell (1933, 224).

(ag) Electrodeposition at high p_{H} yields β -**cobalt**, at low p_{H} a mixture of β and α forms (1932, 262). The β -cobalt becomes cubic above 450° C without change in crystal boundaries; it reverts only on cold rolling or through high temperature annealing (1932, 463).

TABLE I. THE CRYSTAL STRUCTURES OF THE ELEMENTS

<i>Element</i>	<i>Crystal system</i>	<i>Type of structure</i>	a_0	c_0 or α	<i>References</i>
Ag	Cubic	F.c. (a)	4.0772±		1932, 348; 1933, 342;
Silver			0.0002 ¹		1934, 199.
Al	Cubic	F.c. (a) ²	4.0406±		1931, 8; 1932, 336,
Aluminum			0.0002		348; 1933, 342, 420.
As	Hexagonal	As (e)			1934, 295.
Arsenic					
Au	Cubic	F.c. (a)	4.0699±		1932, 348; 1933, 342,
Gold			0.0003 ³		343; 1934, 124, 357.
Be	Hexagonal	C.p. (b),	2.2680±	3.5942±	1932, 329; 1933, 224,
Beryllium		(af)	0.0002	0.0003	319.
Bi ⁴	Hexagonal	As (c)			1930, 369, 434; 1931,
Bismuth					420; 1932, 162.
C ⁵	Hexagonal	(h)			1931, 208.
Graphite					
β -Ca (>450° C)	Hexagonal	(ah)	3.98	6.52	1933, 121, 156; 1934,
Calcium					93.
Cb	Cubic	B.c. (c)	3.294±		1931, 323, 324; 1932,
Columbium			0.001 ⁶		371; 1934, 43.
Cd	Hexagonal	C.p. (b)	2.9736±	5.6058±	1931, 238; 1932, 428a.
Cadmium			0.0005	0.0005 ⁷	
α -Ce	Cubic	F.c. (a)	5.143±		1932, 372.
Cerium			0.004		
β -Co		(ag)			1932, 262.
Cobalt					
α -Cr	Cubic	B.c. (c)	2.8787		1931, 367a; 1932, 369;
Chromium					1934, 125.
Cu	Cubic	F.c. (a)	3.6077±		1932, 348; 1933, 328,
Copper			0.0002 ⁸		342; 1934, 357.
α -Fe	Cubic ⁹	B.c. (c)	2.8607±		1930, 439; 1931, 16;
Iron			0.0002		1932, 62, 336, 369;
					1933, 128, 342; 1934,
					124, 137.

¹ At 600° C, $a_0=4.1276$ A (1934, 199).

² There is no allotropic change up to 600° C (1931, 8; 1933, 420).

³ At 475° C, $a_0=4.1010$ A.

⁴ The thermal expansion from room temperature to the melting point has been carefully measured by X-ray means (1931, 127; 1932, 163; 1934, 120, 121a).

⁵ Photographs of incandescent electrodes show that expansion is all normal to the basal plane.

⁶ From a very ductile preparation of Cb made by thermal decomposition of $CbCl_3$ in vacuo. Other a_0 's are ca 0.01 A larger.

⁷ The other precision measurement (1931, 238) gives lower values: $a_0=2.9724$, $c_0=5.6042$.

⁸ At 475° C, $a_0=3.6514$ A.

⁹ Measurements have been made up to 1100° C (1930, 439; 1933, 128; 1934, 137).

<i>Element</i>	<i>Crystal system</i>	<i>Type of structure</i>	a_0	c_0 or α	<i>References</i>
Ga Gallium	Ortho- rhombic	(<i>j</i>), (<i>v</i>)	4.506	4.506 $b_0 = 7.642$	1932, 282; 1933, 281.
Hg Mercury	Hexagonal	(<i>k</i>), (<i>w</i>)	2.999	70°32' at -46° C	1929, 218; 1932, 209; 1933, 321.
In Indium	Tetragonal	(<i>m</i>), (<i>x</i>)	4.583	4.936	1932, 134; 1933, 429, 527.
Ir Iridium	Cubic	F.c. (<i>a</i>)	3.8312± 0.0005		1932, 348; 1933, 342.
Kr Krypton	Cubic ¹	F.c. (<i>a</i>)	5.69 at 88° K		1930, 428; 1932, 392.
α -La Lanthanum	Hexagonal	C.p. (<i>b</i>)	3.75	6.06	1930, 425; 1932, 372.
β -La ² Lanthanum	Cubic	F.c. (<i>a</i>)	5.296		1933, 528; 1934, 233.
Mg Magnesium	Hexagonal	C.p. (<i>b</i>)	3.2022± 0.0002	5.1991± 0.0004	1932, 428a.
Mn (α , β , γ) Manganese					1931, 411.
Mo Molybdenum	Cubic	B.c. (<i>c</i>)	3.140± 0.001		1932, 348.
α -N ₂ (<35° K) Nitrogen	Cubic	(<i>o</i>)	5.67		1932, 391.
β -N ₂ (>35° K) Nitrogen	Hexagonal	(<i>y</i>)	4.039	6.670	1932, 391, 456; 1934, 272.
Nd Neodymium	Hexagonal	C.p. (<i>b</i>)	3.657	5.88	1932, 372.
α -Ni Nickel	Cubic	F.c. (<i>a</i>)	3.5175 ³		1931, 60; 1932, 62, 348; 1934, 122, 125, 198.
β -Ni Nickel	Hexagonal	C.p. (<i>b</i>), (<i>z</i>)	2.60	4.15	1931, 60.
O ₂ Oxygen	Ortho- rhombic				1932, 316, 391.
Os Osmium	Hexagonal	C.p. (<i>b</i>)	2.716	4.331	1932, 434.
Pb Lead	Cubic	F.c. (<i>a</i>)	4.9396± 0.0003		1931, 420; 1932, 120, 348; 1933, 327, 342; 1934, 192.
Pd Palladium	Cubic	F.c. (<i>a</i>)	3.8823 ₈		1931, 427; 1932, 348; 1933, 342, 343.

¹ There is no X-ray evidence for a structural transition.

² This form appears as a surface layer on the α -material after vacuum annealing at 350° for several days.

³ Another determination, on 99.88% Ni, gives $a_0 = 3.5143$ A.

<i>Element</i>	<i>Crystal system</i>	<i>Type of structure</i>	a_0	c_0 or α	<i>References</i>
Pr Praseodymium	Hexagonal	C.p. (b)	3.657	5.924	1932, 93, 390.
Pt Platinum	Cubic ¹	F.c. (a)	3.9161± 0.0003		1933, 342, 343; 1934, 199.
Re Rhenium	Hexagonal	C.p. (b)	2.7553± 0.0004	4.4493± 0.0003	1931, 3, 4, 305; 1932, 428a.
α -Rh Rhodium	Cubic	(ab)	9.211		1931, 225, 226.
β -Rh Rhodium	Cubic	B.c. (c)	3.7955 ₉		1931, 225; 1932, 348; 1933, 342, 343.
S Sulfur (Plastic form stretched)	Monoclinic	(ac)	26.4	12.32	1930, 119a; 1931, 448; 1932, 447; 1934, 175.
Sb Antimony	Hexagonal	As (e) *			1932, 263.
Se (α -form) Selenium	Monoclinic	(ad)	8.992	11.52	1931, 152, 153; 1934, 136.
Se (β -form) Selenium	Monoclinic	(ad)	12.74	9.25	1934, 136.
Sn (white) Tin	Tetragonal	(s)	5.8194± 0.0003	3.1753± 0.0009	1932, 428a; 1933, 429.
Ta Tantalum	Cubic	B.c. (c)	3.296 ²		1932, 348, 371; 1934, 43.
Tl (α , β) Thallium					1931, 411.
U Uranium	Monoclinic	(ae)	2.829	3.308	1930, 424; 1933, 507.
W Tungsten	Cubic	B.c. (c)	3.1589		1932, 348; 1933, 318; 1934, 187.
W (second form) Tungsten	Cubic	(aa)	5.038		1933, 318.
X Xenon	Cubic	F.c. (a)	6.24 at 88° K		1930, 220a; 1932, 392.
Y Yttrium	Hexagonal	C.p. (b)	3.66 ₁	5.81 ₄	1932, 370.
Zn ⁴ Zinc	Hexagonal	C.p. (b)	2.6589	4.9349	1932, 52, 428a; 1933, 337, 339, 493; 1934, 199.
Zr Zirconium	Cubic	B.c. (c)	3.61 near 862° C		1932, 84, 85.

¹ At 600° C, $a_0 = 3.9383$ A.

² "Explosive" Sb is amorphous; it becomes crystalline on exploding.

* This measurement was made upon a very ductile sample prepared by the thermal dissociation of TaCl₅ in vacuo. Results on other material are higher (3.311 A in 1932, 348).

⁴ At 415° C, $a_0 = 2.6792$ A, $c_0 = 5.0481$ A. There is no structural change up to the melting point.

(ah) The evidence concerning the structure of β -calcium (stable above 450° C) was at first contradictory. It is now known that if the metal is pure it is hexagonal close-packed (b); if impure it may be either hexagonal or body-centered cubic (c) with $a_0 = ca\ 4.33\ \text{A}$.

Alloys

A bibliography of new papers describing X-ray measurements on alloy systems is contained in Table II. The structures that occur in metallic systems are of three kinds: (1) solid solutions of one metal in the lattice of another, (2) definite chemical compounds with atoms combined together in stoichiometric proportions, (3) phases with atoms in fixed geometric array but with compositions that can vary over wide limits. Many examples of the second type are described in succeeding chapters but no attempt has been made to summarize the data about structures (1) and (3).

A few non-metallic compounds such as pyrrhotite (FeS) can contain an excess of one or the other of their atomic components; similar compounds, which we often erroneously, from a structural standpoint, describe as being capable of taking one or both of their constituents into solid solution, are common amongst intermetallic compounds. Within recent years another kind of intermetallic compound, the so-called superlattice compound, has become familiar. A superlattice is a relatively complicated atomic arrangement which arises, as an equilibrium state, through the prolonged annealing of an alloy of stoichiometric atomic composition. Such alloys before annealing are usually solid solutions having their atoms in haphazard distribution. Especially simple superlattices are illustrated by the compounds AuCu and AuCu₃; Sb₂Tl₇ is a more complicated example.

TABLE II. BIBLIOGRAPHY OF ALLOY SYSTEMS

<i>Alloy system</i>	<i>References</i>	<i>Alloy system</i>	<i>References</i>
Ag-Al	1932, 364; 1933, 2, 29; 1934, 1, 139.	Ag-Sn	1931, 326.
Ag-As	1931, 66.	Ag-Zn	1932, 426, 465; 1933, 341.
Ag-Au	1933, 116, 283, 502.	Al-Au	1931, 244.
Ag-Bi	1931, 66.	Al-Co	1931, 105.
Ag-Cd	1931, 436; 1932, 430; 1933, 450.	Al-Cu	1931, 334, 365; 1933, 328, 357, 358, 436, 447, 546; 1934, 211, 282.
Ag-Cu	1930, 3a; 1931, 96, 418; 1932, 306, 477; 1933, 414, 505.	Al-Fe	1932, 63, 64; 1933, 334; 1934, 313, 313a.
Ag-Hg	1931, 313, 367; 1933, 494.	Al-Li	1931, 348.
Ag-Li	1931, 348.	Al-Mg	1931, 396; 1932, 407; 1933, 414; 1934, 238a, 340.
Ag-Pd	1931, 427; 1933, 275.	Al-Mn	1931, 52.
Ag-Rh	1933, 118.	Al-Ti	1931, 114.
Ag-Sb	1931, 66.		

<i>Alloy system</i>	<i>References</i>	<i>Alloy system</i>	<i>References</i>
Al-Zn	1932, 148, 313, 409, 415; 1934, 197, 351.	Cu-Mg	1934, 242.
As-Cu	1929, 205a, 205b.	Cu-Mn	1931, 411.
As-Sn	1934, 295.	Cu-Ni	1931, 474; 1934, 198.
Au-Cd	1932, 442.	Cu-Pd	1932, 292.
Au-Cu	1931, 366, 386; 1932, 178; 1933, 419; 1934, 85a, 357.	Cu-Si	1931, 19, 389.
Au-Fe	1934, 124.	Cu-Sn	1927, 313; 1932, 94, 229, 422, 426; 1933, 253, 268; 1934, 39, 118.
Au-Mn	1934, 40.	Cu-Zn	1930, 370; 1931, 51; 1932, 264, 268, 349, 350, 432, 465; 1933, 141, 168, 339, 340; 1934, 2, 335, 349.
Au-Pd	1931, 427; 1934, 181.		
Au-Pt	1931, 428.	Fe-H ₂	1933, 501.
Au-Rh	1933, 118.	Fe-Hg	1932, 77.
Au-Sb	1931, 326; 1932, 58.	Fe-Mn	1930, 388; 1931, 125, 342, 406; 1933, 486.
Au-Sn	1931, 426; 1932, 58.	Fe-N	1931, 69; 1933, 324, 510; 1934, 44.
		Fe-Ni	1931, 358; 1932, 234; 1933, 76; 1934, 67.
B-Co	1933, 47.	Fe-Si	1933, 516.
B-Fe	1933, 47.	Fe-Sn	1933, 125.
B-Ni	1933, 47.	Fe-V	1930, 456; 1934, 148.
Be-Cu	1933, 464.	Fe-W	1931, 343; 1932, 435.
Bi-Pb	1931, 420; 1932, 246; 1934, 82.	Fe-Zn	1931, 105.
Bi-Sb	1932, 59; 1934, 76.		
Bi-Se	1930, 434.	H ₂ -La	1934, 233.
Bi-Sn	1931, 420; 1932, 246.	H ₂ -Pd	1933, 274, 384.
Bi-Tl	1931, 411; 1934, 193.	H ₂ -Ta	1931, 144; 1934, 212.
		H ₂ -Ti	1931, 144.
C-Cr	1930, 455; 1931, 468; 1932, 197; 1933, 401.	H ₂ -V	1931, 144.
C-Fe	1931, 339, 340, 341, 414; 1932, 225, 281, 474; 1933, 128, 325; 1934, 44, 97, 98, 259, 354.	H ₂ -Zr	1931, 144.
C-Ni	1931, 509; 1933, 415.	Hg-Ni	1932, 77.
Cd-Cu	1931, 51; 1933, 338.	Hg-Sn	1933, 439.
Cd-Hg	1932, 438.		
Cd-Li	1933, 27; 1934, 11, 310.	Ir-Os	1932, 434.
Cd-Mg	1930, 72a.		
Cd-Ni	1931, 105.	Li-Sn	1932, 20.
Cd-Pt	1931, 371.		
Cd-Sb	1930, 379; 1932, 1; 1933, 167.	Mg-Mn	1931, 397.
Cd-Sn	1931, 295.	Mg-Zn	1932, 407; 1933, 238a, 414, 465.
Cd-Zn	1932, 52.	Mn-N	1933, 411.
Ce-H ₂	1934, 233.	Mn-Si	1933, 58; 1934, 337.
Co-Mn	1934, 137.	Mn-Zn	1930, 435; 1931, 346; 1932, 353.
Co-W	1932, 4; 1933, 459.		
Co-Zn	1930, 454; 1931, 105; 1932, 353.	Mo-Ni	1934, 137.
Cr-Fe	1931, 16, 367a; 1932, 369; 1933, 196.		
Cr-Ni	1930, 376; 1934, 125.		
Cu-Fe	1932, 95.		
Cu-Li	1930, 247a.		

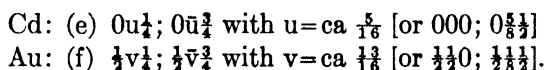
<i>Alloy system</i>	<i>References</i>	<i>Alloy system</i>	<i>References</i>
Na-Pb	1933, 451.	Al-C-Fe	1934, 341.
Na-Tl	1932, 500.	Al-Cr-Fe	1932, 399.
Ni-Zn	1930, 454; 1931, 105; 1932, 200; 1933, 85; 1934, 258.	Al-Cu-Mn	1933, 192, 193; 1934, 26, 107.
		Al-Fe-N	1934, 190.
		Au-H ₂ -Pd	1934, 181.
Pb-Sb	1933, 327.		
Pb-Sn	1933, 327.	Bi-S-Te	1933, 142.
Pb-Tl	1931, 411; 1934, 192.		
Pd-Zn	1931, 105.	C-Co-Fe	1932, 451.
Pt-Zn	1931, 105.	C-Cr-Fe	1931, 468; 1932, 475.
		C-Cr-Ni	1934, 248.
Rh-Zn	1931, 105.	C-Fe-Mn	1932, 15; 1934, 65.
		C-Fe-W	1931, 343.
Sb-Sn	1931, 49, 224; 1933, 425.	Co-Fe-Mn	1933, 263; 1934, 137.
Sb-Tl	1931, 411; 1934, 180.		
Sb-Zn	1933, 167.	Fe-Ni-V	1934, 148.
Sn-Tl	1931, 411; 1933, 215.	Fe-P-Si	1933, 401.
Ag-Cu-Ni	1934, 210.	Al-C-Cr-Mo	1932, 230.
Ag-H ₂ -Pd	1930, 237a; 1933, 275.		

Chapter XIA. Structures of the Type RX

(ac) For some time there was debate as to whether the rhombohedral unit of **AgCN** contains one or two molecules and whether the correct space group is C_{3v}^5 or C_{3v}^6 . A recent recalculation proves that the cell of Table I is monomolecular with C_{3v}^5 as space group and that the atoms are all on trigonal axes with the coordinates (a) uuu. Parameters have not been determined.

AgBr and AgCN form cubic solid solutions; by extrapolation from measurements on them, it can be concluded that cubic AgCN would have $a_0 = 5.69$ Å if it were stable.

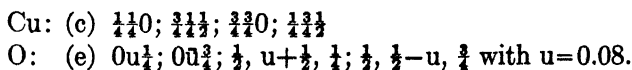
(ad) The low temperature modification of **AuCd**, stable at room temperature, has been assigned a distorted CsCl structure based on the orthorhombic space group V_h^6 . The two molecules in its unit have atoms in the positions:



(ae) The data on **CdLi** are contradictory. One determination gives it the cubic body-centered CsCl structure (a) with $a_0 = 3.32$ Å; the other assigns to it the NaTl superstructure [(ao), below] with $a_0 = 6.687$ Å.

(af) No diffraction lines have been found to give **CsCN** a unit larger than the one-molecule cell. The available experimental data thus indicate that in this cyanide, as in the other alkali cyanides, the CN group functions geometrically as a single atom.

(ag) It has recently been concluded that the triclinic symmetry previously assigned to **CuO** is unnecessarily low. The proposed arrangement, developed from C_{2h}^6 , has atoms in the following positions:



(ah) A new structure, based on photographic data, has been proposed for covellite, **CuS**. It differs from the earlier one (q) mainly in transferring the two sulfur atoms, which were in (a), to the coordinates (c) $\frac{1}{3}\frac{2}{3}\frac{1}{4}$;

TABLE I. THE CRYSTAL STRUCTURES OF THE COMPOUNDS RX

Substance	Symmetry	Structure type	a_0	c_0 or α	References
AgCN	Hexagonal	(k), (ac)	3.88	101°11'	1933, 317; 1934, 288.
AgI	Hexagonal	ZnO (d) ¹	4.580	7.494	1931, 46; 1934, 141.
AgI (low)	Cubic ²	ZnS (c)	6.473		1931, 46; 1934, 141.
AgI (high)	Cubic	(aw)	5.034		1931, 46; 1934, 257.
AgLi	Cubic	CsCl (a)	3.168		1930, 247; 1931, 348; 1933, 523.
AlLi	Cubic		3.23		1931, 348.
AlNd	Cubic	CsCl (a)	3.73		1934, 255.
AuCd (low)	Ortho- rhombic	(ad)	3.144	4.745 $b_0 = 4.851$	1932, 341.
AuCd (high)	Cubic	CsCl (a)	3.34 at 400° C		1932, 341.
AuSn	Hexagonal	NiAs (e)	4.314	5.512	1931, 426; 1932, 58; 1933, 223.
BaNH	Cubic	NaCl (b)	5.84		1934, 103.
BaO	Cubic	NaCl (b)	5.523		1933, 80.
β -CO	Hexagonal	(at)	4.11	6.79	1934, 272.
CaNH	Cubic	NaCl (b)	5.006		1933, 137; 1934, 103.
CaTl	Cubic	CsCl (a)	3.847		1933, 523.
CdLi	Cubic	(ae)	[6.687]		1933, 27, 523.
CdO	Cubic	NaCl (b)	4.689		1931, 272; 1933, 158.
CdSb	Ortho- rhombic	CdSb (n) ³			1930, 379; 1932, 1.
CoS	Hexagonal	NiAs (e)	3.38	5.20	1932, 90.
CsCN	Cubic	CsCl (a), (af)	4.25		1931, 319.
CsCl (low)	Cubic	CsCl (a)	4.20 at ca 450° C		1934, 286.
CsCl (high, >456° C)	Cubic	NaCl (b)	7.10		1933, 485; 1934, 286.
CsHS	Cubic	CsCl (a)	4.29		1934, 287.
CuF	Cubic	ZnS (c)	4.25 ₅		1933, 122.
CuO (Tenorite)	Monoclinic	(o), (ag)	4.66	5.09 $b_0 = 3.40, \beta = 99^\circ 30'$	1933, 479.
CuS (Covellite)	Hexagonal	(q), (ah)	3.76	16.26	1930, 371; 1932, 342.
(Cu, Fe, Mo, Sn) ₄ (S, As, Te) ₂₋₄ (Colusite)	Cubic	ZnS (c)	5.304		1933, 517.
FeO	Cubic	NaCl (b), (ai), (ax)	4.33 ₂		1933, 234, 235; 1934, 77.
FeS	Hexagonal	NiAs (e), (aj)			1932, 253; 1933, 162, 165; 1934, 176.
FeSi	Cubic	(t)			1930, 340a.

¹ $u = 0.371$.² Precipitates with excess of Ag ions.³ According to one analysis there are two forms of CdSb, both hexagonal with identical unit cells (1930, 379).

Substance	Symmetry	Structure type	a_0	c_0 or α	References
GeS	Ortho-rhombic	(<i>ak</i>)	4.29	3.64 $b_0=10.42$	1932, 489.
HBr (low)	Ortho-rhombic (pseudo-cubic)	(<i>al</i>)	5.555	6.063 $b_0=5.64$	1931, 316, 317; 1932, 392; 1933, 315.
HBr (high)	Cubic	HCl (<i>h</i>)	5.76 at -170°C		1931, 316, 317; 1933, 315.
HCl (low)	Ortho-rhombic	(<i>al</i>)	5.03	5.71 $b_0=5.35$	1931, 316, 317; 1933, 315.
HCl (high)	Cubic	HCl (<i>h</i>)	5.46		1931, 316, 317; 1933, 315.
HI	Tetragonal	(<i>am</i>)	6.19	6.68 at 125°K	1931, 316, 317; 1932, 392.
HgF	Tetragonal	Hg ₂ Cl ₂ (<i>g</i>)	3.66	10.9	1933, 122.
HgLi	Cubic	CsCl (<i>a</i>)	3.287		1933, 523.
KCN	Cubic	NaCl (<i>b</i>), (<i>an</i>)	6.51		1931, 319.
KHS (low)	Hexagonal	NaHS (<i>az</i>)	4.374	$68^\circ 51'$	1934, 287.
KHS (high, above ca 170°C)	Cubic	NaCl (<i>b</i>)	6.60		1934, 287.
LiGa	Cubic	NaTl (<i>ao</i>)	6.195		1933, 523.
LiH	Cubic	NaCl (<i>b</i>)			1932, 48.
LiIn	Cubic	NaTl (<i>ao</i>)	6.786		1933, 523.
LiOH	Tetragonal	PbO (<i>f</i>), (<i>ap</i>)	3.546	4.334	1932, 144; 1933, 127.
LiTl	Cubic	CsCl (<i>a</i>)	3.424		1933, 523.
LiZn	Cubic	NaTl (<i>ao</i>)	6.209		1933, 523.
MgPr	Cubic	CsCl (<i>a</i>), (?)	3.88		1933, 387.
MgTl	Cubic	CsCl (<i>a</i>)	3.628		1933, 523.
MgZn	Hexagonal	(<i>aq</i>)	5.33	17.16	1933, 465.
MnO	Cubic	NaCl (<i>b</i>), (<i>ax</i>)			1934, 77.
MnS (red precipitate)	Cubic	ZnS (<i>c</i>)	5.600 ± 0.002		1932, 411; 1933, 417.
MnS (green precipitate)	Cubic	NaCl (<i>b</i>), (<i>ax</i>)	5.212 ± 0.002		1933, 417; 1934, 77.
MnS (red precipitate)	Hexagonal	ZnO (<i>d</i>)	3.976 ± 0.002	6.432 ± 0.004	1932, 411; 1933, 417.
MoC	Hexagonal	(<i>ar</i>)	2.901	2.786	1932, 450.
γ -NH ₄ Br (at -100°C)	Tetragonal	(<i>ap</i>)	6.007	4.035	1934, 132.
NH ₄ HS	Tetragonal	PbO (<i>f</i>), (<i>ap</i>)	6.01	4.01	1934, 287.
NaBi	Tetragonal*		3.46	4.80	1932, 499.
NaCN	Cubic	NaCl (<i>b</i>)	5.83		1931, 319.
NaHS (low)	Hexagonal	NaHS (<i>az</i>)	3.986	$68^\circ 5'$	1934, 287.

* Said to contain one molecule and probably to be body-centered.

<i>Substance</i>	<i>Symmetry</i>	<i>Structure type</i>	a_0	c_0 or α	<i>References</i>
NaHS (high, above ca 90° C)	Cubic	NaCl (b)	6.05		1934, 287.
NaIn	Cubic	NaTl (ao)	7.297		1933, 526.
NaTl	Cubic	NaTl (ao)	7.473		1932, 500.
NiAs	Hexagonal*	NiAs (e)	3.602	5.009	1933, 130.
NiO	Cubic	NaCl (b)	4.1684± 0.0001		1931, 37, 272; 1933, 87.
NiS	Hexagonal				1931, 264.
PbO (red)	Tetragonal	PbO (f)	3.968	5.011	1932, 120.
PbO (yellow)	Ortho-rhombic	(x)	5.459	5.859 $b_0=4.723$	1932, 120.
PtS (Cooperite)	Tetragonal	(av)	3.47	6.10	1932, 17.
(Pt, Pd, Ni)S (Braggite)	Tetragonal	(as)	6.37	6.58	1932, 17.
PtSn	Hexagonal	NiAs (e)	4.103	5.428	1932, 236; 1933, 223.
RbCN	Cubic	NaCl (b)	6.82		1931, 319.
RbHS (low)	Hexagonal	NaHS (az)	4.525	69°20'	1934, 287.
RbHS (high)	Cubic	NaCl (b)	6.93 at ca 200° C		1934, 287.
SbZn	Ortho-rhombic	CdSb (n)	6.17	3.94 $b_0=8.27$	1933, 167.
SiC (II)	Hexagonal	(y), (au)	3.076	15.07	1932, 205; 1933, 59.
SnAs	Cubic	NaCl (b), (ay)	5.681		1934, 295.
SnO	Tetragonal	PbO (f)			1932, 469.
SrNH	Cubic	NaCl (b)	5.45		1934, 103.
SrO	Cubic	NaCl (b)	5.144		1933, 80.
SrTl	Cubic	CsCl (a)	4.024		1933, 523.
TaC	Cubic	NaCl (b)	4.4460± 0.0005		1933, 424; 1934, 42.
TiC	Cubic	NaCl (b)	4.320		1931, 59; 1932, 414; 1934, 42.
TiCN	Cubic	CsCl (a)	3.82		1934, 256a.
TiCl	Cubic	CsCl (a)	The value $a_0=3.380$ in 1933, 302 is undoubtedly a misprint.		
VO	Cubic	NaCl (b)	4.08		1932, 302.
WC	Hexagonal		2.910	2.838	1931, 343.
ZnO	Hexagonal†	ZnO (d)	3.248	5.203	1933, 218.
ZrC	Cubic	NaCl (b)	4.687		1934, 42.

* There is no change in structure below 600° C.

† No change in structure between 110° and 1300° C.

$\frac{2}{3}\frac{1}{3}\frac{1}{3}$. The other atoms are similarly placed in both structures. The new copper parameter $u=0.107$ in (f) $\frac{1}{3}\frac{2}{3}u$; etc. is nearly the same as the old; the sulfur parameter $v=0.062$ in (e) $00v$; etc. is considerably different. This new structure has the atomic separations characteristic of neutral atoms (Cu-S=2.20-2.35 Å, S-S=2.05 Å).

(ai) The values of a_0 for specimens of FeO, which invariably are deficient in iron, increase with the amount of iron present. For an oxide containing 76.08% Fe, $a_0=4.2816$ A; for a sample with 76.72% Fe, $a_0=4.3010$ A. By extrapolation pure FeO (77.73% Fe) would have $a_0=4.332$ A.

(aj) Pyrrhotite has the composition $Fe_{1-x}S_{(1+x)}$ not by reason of the presence of an excess of sulfur but because some of the iron atoms are missing from their structural positions. It is said that pure FeS gives evidence of a superlattice containing 12 molecules; the a_0 of this lattice is the diagonal of a_0 for the simple cell, its c_0 is twice as great: $a_0=5.946$ A, $c_0=11.720$ A.

Ordinary pyrrhotite ($a_0=3.41$ A, $c_0=5.72$ A) becomes ferromagnetic if heated above 200° C; this form, giving $a_0=3.47$ A, $c_0=5.84$ A at room temperature, reverts to the non-magnetic form if heated above 450° C (1934, 176).

(ak) From photographic data it has been concluded that the four molecules of GeS are in special positions (c) of the space group V_h^{16} :

$$\text{Ge: (c) } uv0; \bar{u}, \frac{1}{2}-v, \frac{1}{2}; u+\frac{1}{2}, \bar{v}, \frac{1}{2}; \frac{1}{2}-u, v+\frac{1}{2}, 0$$

$$\text{with } u=0.167, v=-0.125$$

$$\text{S: (c) } u'v'0; \text{ etc. with } u'=v'=0.111.$$

The axes $X'Y'Z'$ of 1930, 352 bear the following relation to the axes abc of this description: $a=Z'$, $b=Y'$, $c=X'$. The kind of packing that prevails is illustrated by Figure 276a and b.

FIG. 276a.—The unit cell of the structure of GeS projected on an a -face. The large circles are sulfur.

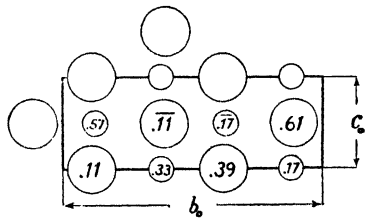
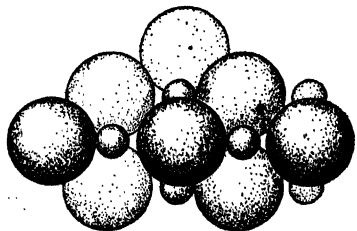


FIG. 276b.—A packing drawing of a with Ge and S atoms given their ionic sizes. In making these packing drawings it is sometimes better to show an atom at a height $1+x$ instead of the equivalent atom of height x . Thus in this figure the central sulfur atom is at $1-0.11=0.89$ (and not at -0.11). Similarly its neighboring Ge is at 0.83 instead of -0.17 , as in a .



(al) Earlier work described the low temperature modifications of **HCl** and **HBr** as tetragonal. The more recent experiments, however, make them orthorhombic pseudo-cubic with four molecules in the unit. The space group of low HBr is thought to be either V^7 or V_h^{23} .

(am) Cubic **HI** is not cubic, as first stated, but tetragonal. It is said that its transitions do not involve atomic rearrangements.

(an) A reexamination of **KCN** has failed to supply data indicating a unit larger than that of the four-molecule NaCl-like grouping.

(ao) The **NaI** superlattice, found for a number of alloys, contains eight molecules with atoms in the following special positions of O_h^7 :

$$\begin{array}{l} \text{TI: (8f) } 000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4} \\ \text{Na: (8g) } \frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}. \end{array}$$

(ap) Three additional crystals have been found to have the PbO (*f*) type of structure but with parameters and cells so different that other atomic relationships are produced.

Of these substances **LiOH** is most like PbO. Lithium atoms are in (a) 000; $\frac{1}{2}\frac{1}{2}0$, OH groups are at (c) $0\frac{1}{2}u$; $\frac{1}{2}0\bar{u}$ with *u* said to be 0.20. If *u* is really so small there is a surprisingly large separation (ca 3.5 Å) between the OH ions of adjacent layers.

The other two crystals with this grouping, **NH₄HS** and the γ -form of **NH₄Br**, photographed at -100°C , have identical units. Since in most compounds the HS ion has practically the same size as the bromide ion, it might be expected that the parameters defining them would be little different. In view of this fact it will be interesting to learn from future work whether the unlike parameters found for the bromide and hydrosulfide are both right. Expressing the atomic positions in the coordinates used for LiOH (above) and for PbO, $u(\text{HS})=0.66$ for **NH₄HS**; for γ -**NH₄Br**, $u(\text{Br})=0.53$. A drawing of the bromide is reproduced in Figure 277a and b for comparison with the PbO packing illustrated in Figure 176.

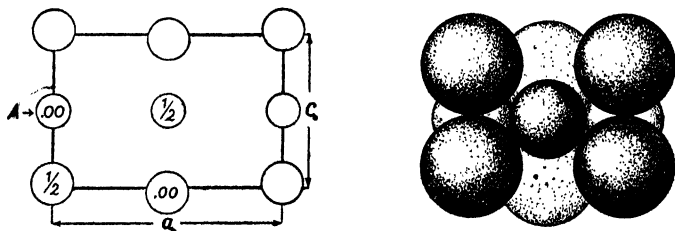


FIG. 277a.—(left) The variant of the tetragonal PbO (*f*) arrangement provided by the γ -form of **NH₄Br**. Small circles are **NH₄** groups; the origin is in the **NH₄** ion at A.

FIG. 277b.—(right) A packing drawing of γ -**NH₄Br** with the **NH₄** group shown as the smaller sphere. It is evident that good packing results if, as in this drawing, the atoms are given their usual ionic sizes.

(ag) It is said that the structure of **MgZn** resembles that of **MgZn₂** [see Chapter XII, (ab)] with two magnesium atoms in place of zinc atoms and with c_0 doubled in length.

(ar) The molybdenum atom of the single **MoC** molecule in the unit is at the origin (000); the carbon atom is thought to be at $\frac{1}{3}\frac{2}{3}\frac{1}{2}$.

(as) The cell of **braggite** is reported to contain eight molecules and to have an arrangement based on D_{4h}^2 . The sample that was studied contained 20% Pd and 5% Ni.

(at) The β -form of **CO**, stable above 61.5° K, has the same structure as β -nitrogen. If the arrangement found for β -N₂ is correct, this modification of CO, too, has rotating molecules in close-packed array.

(au) A Fourier analysis has been made of the basal reflections from an unspecified type of **SiC** (1932, 205).

(av) The tetragonal cell of the mineral **cooperite**, **PtS**, has been described as containing two molecules. Its atoms are thought to be in the following special positions of D_{4h}^9 : Pt: (c) $0\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$, S: (e) $00\frac{1}{4}$; $00\frac{3}{4}$.

(aw) The unit cube of the modification of **AgI** stable above 146° C is supposed to contain two molecules. Iodine atoms are reported to be at 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; silver is described as occupying two of the 30 largest holes resulting from this iodine packing. Such an unusual structure needs further confirmation.

(ax) Measurements of a_0 for cubic **MnO** at low temperatures show that there is no change in structure around 160° K where an anomalous heat change occurs. At this point there is, however, a minimum in the cubic edge length. Magnetite, **Fe₃O₄**, behaves similarly. **MnS** and **FeO** likewise do not have different crystal structures above and below the temperatures at which they show thermal anomalies. Neither do they have a region in which they contract on warming; instead they show two different rates of thermal expansion. The data for these conclusions are given in Table II.

TABLE II. VALUES OF a_0 AT SEVERAL TEMPERATURES

Temperature	a_0 for Compound			
	<i>MnO</i>	<i>Fe₃O₄</i>	<i>MnS</i>	<i>FeO</i>
299° K	4.436	8.363	5.210	4.290
200	—	—	—	4.286
186	—	—	—	4.284
160	4.409	8.357	5.204	4.283
143	—	—	5.204	—
138	—	—	5.197	—
130	—	—	5.192	—
114	4.416	8.363	—	—
104	4.419	8.363	—	—

(ay) The compound SnAs is especially interesting in being an example of the NaCl grouping which is capable of "dissolving" both components, the As-rich limit being at 49% As, the Sn limit at 34.5% As. The pure compound has the lowest value of a_0 .

(az) The one-molecule rhombohedron of the form of the alkali hydro-sulfides stable at room temperatures is very different in shape from that found for AgCN . Atomic parameters are not known for any of these crystals.

Chapter XIIA. Structures of the Type RX_2

(as) The monoclinic unit of Ag_2Te has been said to contain three molecules; this is improbable. A sample heated to $250^\circ C$ and cooled in nitrogen showed no change in pattern.

(at) The diffraction lines of BeF_2 , which were not very sharp, are reported to be those of a tetragonal high cristobalite-like (ae , bd) structure containing eight molecules.

(au) The atomic arrangement assigned to COS on the basis of low temperature powder photographs is developed from C_{3v}^5 . The atoms in its single molecule rhombohedron are on three-fold axes with the coordinates uuu . For C , $u=0$; for S , $u'=0.336$; for O , $u_1=-0.187$. The resulting interatomic distances within the molecule are $C-O=1.10$ A, $C-S=1.96$ A; between different molecules $O-S=2.78$ A.

(av) The astonishingly large unit assigned to Cu_2S would contain 160 molecules.

(aw) **Marcasite (FeS_2)** and **löllingite ($FeAs_2$)** have been given smaller unit cells. These cells contain two molecules with atoms arranged according to V_h^{12} . Iron atoms are in (a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, sulfur (or arsenic) atoms in (g) $0uv$; $0\bar{u}\bar{v}$; $\frac{1}{2}$, $\frac{1}{2}-u$, $v+\frac{1}{2}$; $\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}-v$. The axes, abc , of this description and $X'Y'Z'$ of 1930, 352 are connected by the relation $a=Z'$, $b=X'$, $c=Y'$. For FeS_2 , $u=0.203$, $v=0.375$; for $FeAs_2$, $u'=0.175$, $v'=0.361$; for the more recently studied phosphide FeP_2 , $u''=0.16$, $v''=0.37$. The grouping of marcasite, as typical of this structure, is illustrated in Figure 278a and b. It consists of open meshworks of iron atoms and

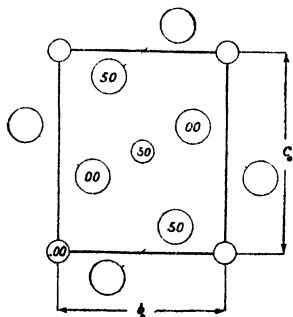


FIG. 278a.—(left) The new atomic arrangement deduced for marcasite, FeS_2 , as projected upon the a -face of its orthorhombic cell. The small circles are Fe atoms.

FIG. 278b.—(right) A packing drawing of FeS_2 if Fe and S are shown with the radii of their neutral atoms. The line-shaded atoms are Fe.

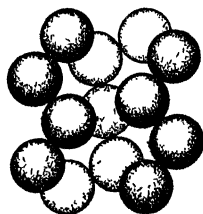


TABLE I. THE CRYSTAL STRUCTURES OF THE COMPOUNDS RX_2

Substance, symmetry and structure type			a_o	c_o or a	References
Ag ₂ S (Acanthite)	Ortho- rhombic	(bf)	4.77	6.88	1931, 124, 345.
Ag ₂ S (Argentite)	Cubic	Cu ₂ O (j), above 180° C (bf)	4.90	$b_o=6.92$	1931, 124, 345.
Ag ₂ Te	Monoclinic	(as)	5.98	5.56	1932, 444.
				$b_o=6.31, \beta=75^\circ 2'$	
Al ₂ Au	Cubic	CaF ₂ (a)	6.00		1932, 292.
AlCuMg	Hexagonal	MgZn ₂ (ab)	5.09	8.35	1934, 339.
Au ₂ Pb	Cubic	MgCu ₂ (q)	7.91		1934, 209a.
AuSb ₂	Cubic	FeS ₂ (f)	6.647		1931, 326; 1932, 58; 1933, 223.
BaF ₂	Cubic	CaF ₂ (a)	6.187		1933, 422.
Be ₂ C	Cubic	CaF ₂ (a)	4.33		1931, 425; 1934, 354b.
Be ₂ Cu	Cubic	MgCu ₂ (q)	5.94		1934, 339.
BeF ₂	Tetragonal	(at)	6.60	6.74	1932, 70.
Be ₂ Fe	Hexagonal	MgZn ₂ (ab)	4.22	6.83	1934, 339.
CO ₂	Cubic	CO ₂ (g), (bg)	5.575 at -190° C		1931, 458, 459; 1934, 130, 130a.
COS	Hexagonal	(au)	4.08	98°58'	1931, 457.
				at liquid air temp.	
CaF ₂	Cubic	CaF ₂ (a)	5.451		1933, 422.
CaI ₂	Hexagonal	CdI ₂ (c), (bi)	4.48	6.96	1933, 52.
CdBr ₂	Hexagonal	(bn)			1933, 43.
CdCl(OH)	Hexagonal	(bh)	3.66	10.27	1934, 110.
CdI ₂		(c), (bi)			1932, 8; 1933, 174.
CoCl ₂	Hexagonal*	CdCl ₂ (e)	6.16	33°26'	1934, 95.
CuF ₂	Cubic	CaF ₂ (a)	5.406		1933, 122.
Cu ₂ Mg	Cubic	(q), (bs)			1934, 242.
Cu ₂ O	Cubic	Cu ₂ O (j)	4.252		1931, 321, 322; 1932, 483.
Cu ₂ S	Ortho- rhombic	(av)	11.8	22.7	1930, 371.
				$b_o=27.2$	
FeAs ₂	Ortho- rhombic	FeAs ₂ (i), (aw)	2.85	5.92	1932, 83.
				$b_o=5.25$	
Fe ₂ B	Tetragonal	(t), (bp)			1930, 116a; 1931, 146.
FeOCl	Ortho- rhombic	(bj)	3.75	3.3	1934, 84.
				$b_o=7.95$	
FeP ₂	Ortho- rhombic	FeAs ₂ (aw)	2.725	5.657	1934, 173.
				$b_o=4.975$	
FeS ₂	Cubic	FeS ₂ (f), (bk)	5.405		1932, 352.
FeS ₂	Ortho- rhombic	FeAs ₂ (i), (aw)	3.37	5.39	1931, 71.
				$b_o=4.44$	
GeO ₂	Tetragonal†	SnO ₂ (b)	4.390	2.895	1932, 164.

("Insoluble" form)

* For CoCl₂, $u=0.25$.† Parameter $u=0.3$.

Substance, symmetry and structure type			a_0	c_0 or a	References
H ₂ O	Hexagonal	(<i>x</i>), (<i>bl</i>)	4.508	7.338 at -66° C	1933, 257; 1934, 16.
H ₂ S	Cubic	(<i>al</i>), (<i>ax</i>)			1931, 315, 456.
H ₂ Se	Cubic	(<i>al</i>), (<i>ax</i>)			1931, 315, 456.
HgBr ₂	Ortho- rhombic	(<i>ay</i>)	6.85	12.45 $b_0=4.67$	1931, 461; 1932, 66.
HgCl ₂	Ortho- rhombic	(<i>y</i>), (<i>bm</i>)	5.963	4.324 $b_0=12.735$	1932, 332; 1934, 316.
HgF ₂	Cubic	CaF ₂ (<i>a</i>)	5.54		1933, 122.
HgI ₂	Ortho- rhombic	HgBr ₂ (<i>ay</i>)	7.32	13.76 $b_0=4.674$	1934, 85.
KBi ₂	Cubic	Cu ₂ Mg (<i>q</i>)	9.501		1932, 501.
K ₂ O	Cubic	CaF ₂ (<i>a</i>)	6.436		1934, 309.
K ₂ S	Cubic	CaF ₂ (<i>a</i>)	7.391		1934, 287, 309.
K ₂ Se	Cubic	CaF ₂ (<i>a</i>)	7.676		1934, 309.
K ₂ Te	Cubic	CaF ₂ (<i>a</i>)	8.152		1934, 309.
Li ₂ O	Cubic	CaF ₂ (<i>a</i>)	4.619		1934, 309.
Li ₂ S	Cubic	CaF ₂ (<i>a</i>)	5.708		1934, 309.
Li ₂ Se	Cubic	CaF ₂ (<i>a</i>)	6.005		1934, 287, 309.
Li ₂ Te	Cubic	CaF ₂ (<i>a</i>)	6.504		1934, 287, 309.
Mg ₂ Ge	Cubic	CaF ₂ (<i>a</i>)	6.378		1933, 525.
MgI ₂	Hexagonal	CdI ₂ (<i>c</i>), (<i>bi</i>)	4.14	6.88	1933, 52.
MgNi ₂	Hexagonal	MgZn ₂ (<i>ab</i>)	4.81	7.95	1934, 339.
MgNiZn	Cubic	MgCu ₂ (<i>q</i>)	6.96		1934, 339.
Mg ₂ Pb	Cubic	CaF ₂ (<i>a</i>)	6.836		1933, 525.
Mg ₂ Sn	Cubic	CaF ₂ (<i>a</i>)	6.765		1933, 525.
MgZn ₂	Hexagonal	(<i>ab</i>)			1934, 260.
MnS ₂ (Hauerite)	Cubic	FeS ₂ (<i>f</i>)	6.097*		1932, 346, 411; 1933, 417; 1934, 204, 346.
Mo ₂ C	Hexagonal	(<i>az</i>)	2.994	4.722	1932, 450.
N ₂ O	Cubic	CO ₂ (<i>g</i>)	5.656		1931, 458, 459.
NO ₂	Cubic	(<i>an</i>), (<i>ba</i>)			1931, 170, 454, 455.
Na ₂ S	Cubic	CaF ₂ (<i>a</i>)	6.526		1934, 309.
Na ₂ Se	Cubic	CaF ₂ (<i>a</i>)	6.809		1934, 309.
Na ₂ Te	Cubic	CaF ₂ (<i>a</i>)	7.314		1934, 309.
NdC ₂	Tetragonal	CaC ₂ (<i>k</i>)	3.81	6.36	1931, 425.
NiBr ₂	Hexagonal	CdCl ₂ (<i>e</i>), (<i>bn</i>)	6.46	33°20'	1934, 134.
NiI ₂	Hexagonal	CdCl ₂ (<i>e</i>)	6.92	32°40'	1934, 134.
Ni(OH) ₂	Hexagonal	CdI ₂ (<i>c</i>)	3.114	4.617	1933, 87.
OsS ₂	Cubic	FeS ₂ (<i>f</i>)	5.6075± 0.0006		1934, 174.
PbBr ₂	Ortho- rhombic	PbBr ₂ (<i>y</i>), (<i>bb</i>)			1932, 332.
PbFBr	Tetragonal	PbFBr (<i>bc</i>)	4.18	7.59	1932, 331.
PbCl ₂	Ortho- rhombic	(<i>y</i>), (<i>bb</i>)	4.525	9.030 $b_0=7.608$	1931, 302; 1932, 69.
PbFCl	Tetragonal	(<i>bc</i>)	4.09	7.21	1932, 330; 1933, 323; 1934, 9.

* $u=0.4012$.

Substance, symmetry and structure type			a_o	c_o or a	References
α -PbF ₂	Ortho-rhombic	(y), (bb)	3.80	7.61	1932, 269; 1933, 422.
β -PbF ₂	Cubic*	CaF ₂ (a)	5.942±0.002	b _o =6.41	1933, 422.
PbO ₂	Tetragonal	SnO ₂ (b)	4.931	3.367	1932, 120.
PdF ₂	Tetragonal	SnO ₂ (b)	4.93	3.38	1931, 100.
PrC ₂	Tetragonal	CaC ₂ (k)	3.85	6.41	1931, 425.
PtAs ₂ (Sperrylite)	Cubic	FeS ₂ (f), (br)			1932, 17.
RuS ₂ (Laurite)	Cubic	FeS ₂ (f), (br)	5.59		1932, 17.
SaC ₂	Tetragonal	CaC ₂ (k)	3.75	6.28	1931, 425.
SiO ₂ (α -Quartz, low)	Hexagonal	(l)	4.9029	5.3933	1930, 375; 1933, 62, 232, 277; 1934, 121a.
SiO ₂ (α -Cristobalite, low)	Ortho-rhombic	(bq)	7.00	7.00	1932, 25.
SiO ₂ (β -Cristobalite, high)	Cubic	(ae), (bd)		b _o =7.00	1932, 24.
SrC ₂	Tetragonal	CaC ₂ (k)	4.11†	6.68	1930, 299.
SrF ₂	Cubic	CaF ₂ (a)	5.784		1933, 422.
Ta ₂ C	Hexagonal	(az)	3.091	4.93	1934, 42.
YC ₂	Hexagonal	(bo)	3.79	6.58	1931, 425.
Zn(OH) ₂	Hexagonal	CdI ₂ (c), (?) (be)	3.14	ca 5.12	1932, 146a.
Zn(OH) ₂	Ortho-rhombic	(ai), (be)	8.53	4.92	1933, 104.
ZrW ₂	Cubic	Cu ₂ Mg (g)	7.61	b _o =5.16	1933, 95.

* Transition between 220°–280° C.

† $a_o=5.81$ Å as given in book, p. 239, applies to a larger diagonal cell.

sulfur pairs layered normal to the a-axes. The atomic contacts are perfect if iron and sulfur are given their radii as neutral atoms.

(ax) The patterns of H₂S and H₂Se indicate that the sulfur and selenium atoms are in face-centered array; nothing can of course be told about the hydrogen positions.

(ay) The four molecules in the unit of HgBr₂ are arranged according to the space group C_{2v}¹². All atoms are in special positions (a) u0v; \bar{u} , 0, $v+\frac{1}{2}$; $u+\frac{1}{2}$, $\frac{1}{2}$, v; $\frac{1}{2}-u$, $\frac{1}{2}$, $v+\frac{1}{2}$, with the parameters: for Hg, $u=0.334$, $v=0$; for Br', $u'=0.056$, $v'=0.132$, for Br'', $u''=0.386$, $v''=0.366$. As Figure 279 shows, this arrangement is a typical layer-like structure, contact between the layers being maintained through bromine atoms. If the atoms are given their usual ionic sizes, as in the packing drawing, excellent contacts result.

Yellow mercuric iodide apparently has this $HgBr_2$ grouping.

(az) The two molybdenum atoms in the unit cell of Mo_2C are said to be at $\frac{1}{3}\frac{2}{3}\frac{1}{4}$; $\frac{2}{3}\frac{1}{3}\frac{1}{4}$; it is thought that the carbon atom may be at the origin 000. A tantalum carbide, Ta_2C , has the same hexagonal close-packing of its metal atoms; like W_2C it has a second modification.

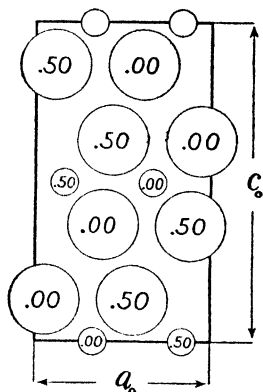


FIG. 279a.—(left) The layer structure of $HgBr_2$ projected on the b -face of its orthorhombic unit. The large circles are Br.

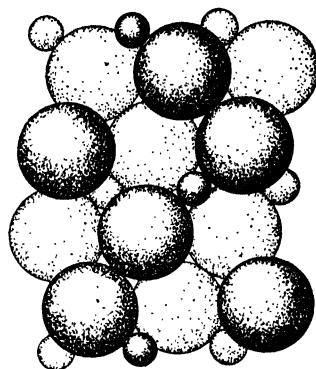


FIG. 279b.—(right) A packing drawing of $HgBr_2$ with the atoms having their ionic sizes.

(ba) The unit cube of solid NO_2 contains 12 molecules. Two conflicting structure types have been proposed using the same data (1931, 454). In one of these, based on T^5 , the nitrogen atoms are in (12c) $u0\frac{1}{2}$; etc. with $u=0.40_3$, the oxygen atoms in general positions xyz ; etc. with $x=0.17_8$, $y=0.25$, $z=0.40_3$. This gives NO_2 molecules with an N-O separation of 1.38 Å. The other discussion proceeds on the assumption that the solid ought to show N_2O_4 molecules. It is pointed out (1931, 170) that this can result if the space group is T^8 with oxygen atoms in general positions and nitrogen atoms in (12a) or (12b). The atomic positions have not been determined for such an arrangement but it is considered that the evidence favors planar molecules.

(bb) In the structures found for $PbBr_2$ and $PbCl_2$ all the atoms are in special positions (c) of V_h^{16} : $0uv$; $\frac{1}{2}$, $\frac{1}{2}-u$, \bar{v} ; 0 , $u+\frac{1}{2}$, $\frac{1}{2}-v$; $\frac{1}{2}$, \bar{u} , $v+\frac{1}{2}$. In $PbBr_2$, $u(Pb)=0.01_6$, $v(Pb)=0.08_7$; for Br' , $u'=0.61$, $v'=0.07_8$, for Br'' , $u''=0.23$, $v''=-0.17$. The different parameters given to the atoms in $PbCl_2$ are to be attributed to the choice of another origin. These parameters are: for Pb, $u=0.25_4$, $v=0.09_5$; for Cl' , $u'=0.65$, $v'=0.07$, for Cl'' , $u''=0.55$, $v''=0.67$. The extreme layer-like nature of the structure possessed by both salts is illustrated by Figure 280; in b the atoms have been drawn with their customary ionic sizes. The packing is far less perfect than that found for $HgBr_2$ (Figure 279); but very possibly more accurate intensity data upon these lead salts would alter the chosen parameters enough to give them better ionic contacts.

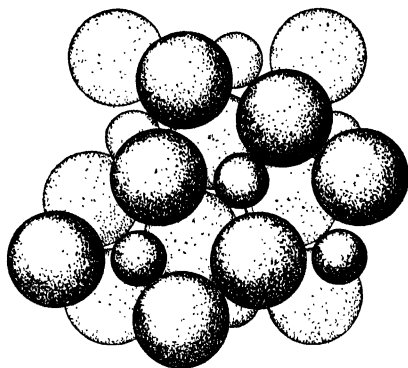
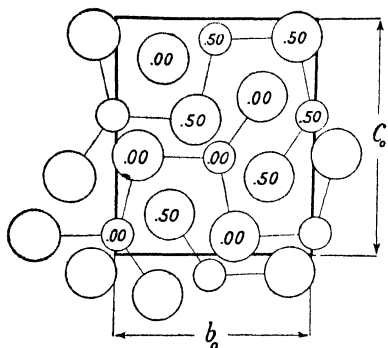


FIG. 280a.—(left) An a-face projection of the PbBr_2 arrangement. The small circles are the Pb atoms. All atoms are in layers normal to the a-axis.

FIG. 280b.—(right) A packing drawing of PbBr_2 with the atoms given their ionic sizes.

(bc) Photographic data have been used to show that the atoms in the two-molecule units of PbFBr and PbFCl are in the following special positions of D_{4h}^7 :

$$\text{Pb: (c) } 0\frac{1}{2}u; \frac{1}{2}0\bar{u}, \text{ Br(or Cl): (c) } 0\frac{1}{2}v; \frac{1}{2}0\bar{v}, \text{ F: (a) } \frac{1}{2}\frac{1}{2}0; 000.$$

For PbFBr , $u=0.195$, $v=0.65$; for PbFCl , $u'=0.20$, $v'=0.65$ (Figure 281).

The mineral matlockite is not $\text{Pb}_2\text{Cl}_2\text{O}$ but PbFCl with the structure described above.

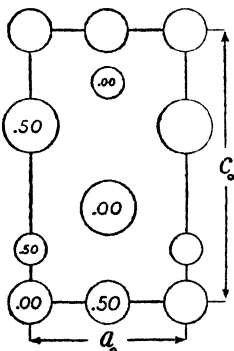


FIG. 281a.—(left) The unit cell of the PbFCl arrangement projected upon one of its tetragonal a-faces. The atom at the origin is F. The largest circles represent Cl atoms, the smallest Pb atoms.

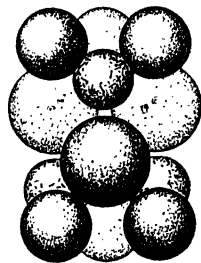


FIG. 281b.—(right) A packing drawing of PbFCl if the atoms have their ionic sizes. The line-shaded spheres are Pb ions.

(bd) It is said that certain faint lines occur in the pattern of **high cristobalite**, SiO_2 , which are not predicted by the holohedral structure (ae). A tetartohedral variant of this arrangement has accordingly been proposed in which the silicon atoms are in two sets of special positions (4f) of T^4 : $uuu; u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}; \bar{u}, u+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-u, \bar{u}, u+\frac{1}{2}$ with $u=0.25_8$ and $u'=-0.00_8$.

of a distorted tetrahedron of (OH) groups; each hydroxyl belongs to two such $\text{Zn}(\text{OH})_4$ sphenoids. The result is a tetrahedral network somewhat resembling those found for the various forms of silica.

A hexagonal modification of $\text{Zn}(\text{OH})_2$ has been said to exist with a CdI_2 (c) structure (1932, 146a). The available experimental evidence is not, however, satisfactory.

(bf) Above 180°C Ag_2S is cubic with the Cu_2O (j) structure; below this temperature the observed pattern is variously described as orthorhombic, like acanthite (1931, 124) and as a mixture of the acanthite and cubic patterns (1931, 345). Four molecules are contained in the acanthite unit described in Table I.

(bg) A reinvestigation of solid CO_2 leads, as before, to the pyrite-like arrangement (f) with $u=0.116$. This gives a C-O distance of 1.13 Å. Recent measurements of a_0 between 20° and 114°K can be expressed by the equation $a_0 = 5.540 + (4.679 \times 10^{-6})T^2$.

(bh) The two-molecule cell of $\text{CdCl}(\text{OH})$ has an atomic arrangement based on C_{6v}^4 . Cadmium and chlorine are in special positions (b) $\frac{1}{2}\frac{2}{3}u$; $\frac{2}{3}$, $\frac{1}{3}$, $u+\frac{1}{2}$ with u (Cd)=0 and u' (Cl)=0.337. Hydroxyl groups are in (a) $00v$; $0, 0, v+\frac{1}{2}$ with $v=0.100$. This gives rise to the interionic contacts pictured in Figure 284a, b and c.

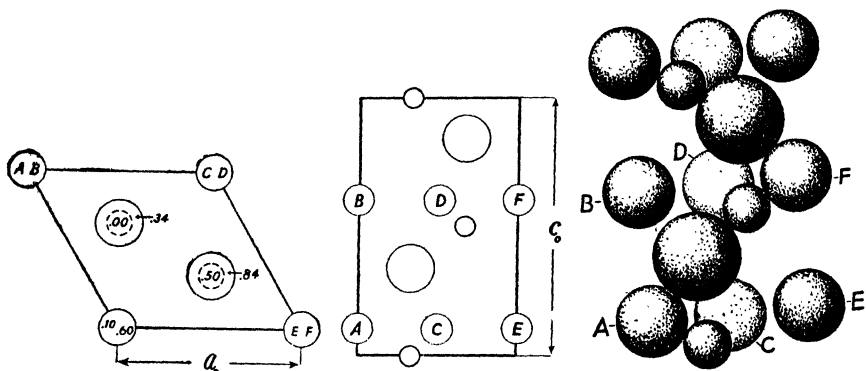


FIG. 284a.—(left) A basal projection of the $\text{Cd}(\text{OH})\text{Cl}$ arrangement. Cd, (OH) and Cl are represented by circles of increasing size. Letters refer to corresponding atoms in Figures 284b and 284c.

FIG. 284b.—(center) A diagonal (11·0) face projection of $\text{Cd}(\text{OH})\text{Cl}$.

FIG. 284c.—(right) A packing drawing of b with the atoms of $\text{Cd}(\text{OH})\text{Cl}$ having their ionic sizes.

(bi) Lines have been found on powder and rotation photographs of CdI_2 which indicate that the c-axis of the one-molecule cell should be doubled. It has been concluded that the atoms in this two-molecule cell are in the positions: Cd: 000 ; $\frac{1}{2}\frac{2}{3}\frac{2}{3}$, I: $\frac{1}{2}\frac{2}{3}u$; $\frac{2}{3}\frac{1}{3}u$; $0, 0, u+\frac{1}{2}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}-u$. It would seem to be proved that under certain circumstances CdI_2 can crystallize with this larger unit, but it is not clear whether it always has such a

complicated structure and the existing data are insufficient to establish the new atomic arrangement. Additional work is especially needed since the original one-molecule structure (c) has been found to satisfy the diffraction data from a large number of different compounds. The additional lines calling for a larger unit have not been recorded from these other CdI_2 -like crystals: some should show them clearly, others would not be expected to do so because of the relative scattering powers of their atoms.

(bj) It has been proposed that the atoms in the two-molecule unit of $FeOCl$ are arranged according to the demands of the space group V_h^{18} . Oxygen and chlorine are placed in (a) $0u0$; $\frac{1}{2}\bar{u}\frac{1}{2}$ [interchange of Y and Z from 1930, 352] and iron in (b) $0v\frac{1}{2}$; $\frac{1}{2}\bar{v}0$ with $u(O) = -0.083$, $u(Cl) = 0.305$, $v = 0.097$. So many crystals have in the past been incorrectly assigned to V_h^{18} that data far more complete and convincing than those yet published for $FeOCl$ are highly desirable. It is also probable that the true atomic arrangement will be found to provide interatomic distances that differ somewhat from those of the structure outlined above.

(bk) A Fourier analysis has been made of quantitative intensity data from crystals of **pyrite** (FeS_2). This leads to a parameter $u(S) = 0.386$. The resulting atomic separations are $S-S = 2.14$ Å, $S-Fe = 2.26$ Å.

(bl) Within the limits of experimental error (± 0.004) the dimensions of ice composed of heavy hydrogen are identical with those of ordinary ice. Structures have been proposed for ice which assign positions to its hydrogen atoms (see 1933, 257); the results of X-ray determinations of course have nothing to say about such speculations.

(bm) From photographic data $HgCl_2$ has recently been given a structure which is considered to be essentially molecular. Like $PbBr_2$ and $PbCl_2$ (bb), all atoms are in special positions (c) of V_h^{16} : $0uv$; $\frac{1}{2}$, $\frac{1}{2}-u$, \bar{v} ; 0 , $u+\frac{1}{2}$, $\frac{1}{2}-v$; $\frac{1}{2}$, \bar{u} , $v+\frac{1}{2}$. The parameters found for them are $u(Hg) = 0.376$, $v = 0.053$; $u'(Cl') = 0.517$, $v' = 0.375$; $u''(Cl'') = 0.742$, $v'' = 0.778$. The

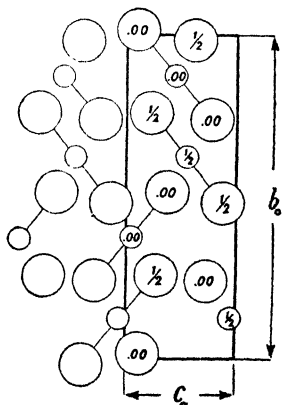
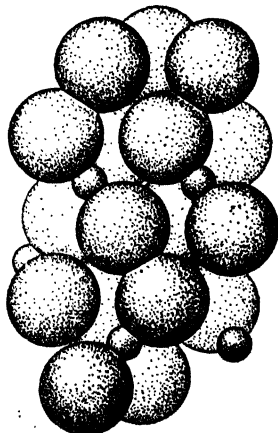


FIG. 284d.—(left) The structure found for $HgCl_2$ projected upon an a-face. Large circles are Cl atoms.

FIG. 284e.—(right) The type of packing that prevails in the $HgCl_2$ arrangement if atoms are given their ionic radii. In this drawing the atomic layer at $\frac{1}{2}$ in d is on top.



type of packing provided by this arrangement if the atoms have their usual ionic sizes is illustrated in Figure 284d and e. The nearest approach of Hg and Cl atoms is 2.25 Å; Cl-Cl is 3.4 Å.

(bn) NiBr₂ obtained by sublimation has the CdCl₂ arrangement (e) with $u(\text{Br})=0.255$. The compound made by dehydration, by driving NH₃ from the hexammoniate or by recrystallization from alcohol is a "Wechselstruktur." The pattern for this gives $a_0=2.11$ Å, $c_0=6.08$ Å, a hexagonal cell which would contain only a third of a molecule. It has been proposed that these results can be interpreted in terms of an intimate twinning of CdCl₂ and CdI₂ structures—a few layers of each together. CdBr₂ has been found to give a similar "Wechselstruktur" with $a_0=2.30$ Å, $c_0=6.23$ Å; NiI₂ on the other hand seems always to have the CdCl₂ arrangement.

(bo) The structure of YC₂ is different from that of the other carbides studied. It is supposed to be hexagonal with a two-molecule cell.

(bp) A new structure has been proposed for Fe₂B which differs from the previous one (t) in the parameters assigned to the Fe atoms at (i) of V_a¹¹ and in the positions thought probable for the boron atoms. Borons are placed at (c) $\frac{1}{2}00$; $0\frac{1}{2}\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$ instead of (a) and (b), and for Fe, $u=\frac{1}{8}$ and $v=\frac{1}{4}$ instead of $\frac{1}{2}$ (Figure 285). If $v=\frac{1}{4}$ is exactly correct the structure is identical with the one found for CuAl₂ (n), with a change of origin to $0\frac{1}{2}0$.

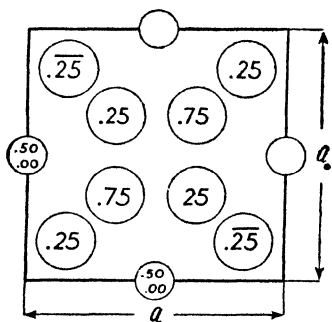


FIG. 285a.—(left) A basal projection of the new arrangement proposed for Fe₂B. The large circles are the Fe atoms.

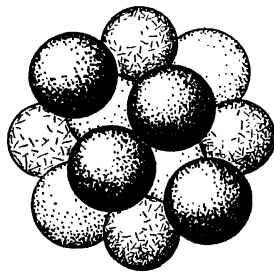


FIG. 285b.—(right) A packing drawing of a if the Fe atoms are assumed to be neutral and if the (line-shaded) boron is given a size probable for its neutral atoms.

(bq) It is suggested that the unit cell of the room temperature (low) modification of cristobalite contains eight molecules and that the atomic arrangement, based on V⁴, is a distortion of that of high cristobalite (compare Figure 286 with Figures 282 and 194a). All atoms are in general positions: xyz ; $x+\frac{1}{2}$, $\frac{1}{2}-y$, \bar{z} ; \bar{x} , $y+\frac{1}{2}$, $\frac{1}{2}-z$; $\frac{1}{2}-x$, \bar{y} , $z+\frac{1}{2}$. Parameters which

Chapter XIII A. Structures of the Type R_2X_3

(m) A complex arrangement which includes a place for one sodium atom per cell has been proposed for $\beta\text{-Al}_2\text{O}_3$. Based on D_{6h}^4 it has atoms in the following positions:

- 1 Na+1 Al: (a) 000; $00\frac{1}{2}$
 4 Al: (f) $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}$; $\frac{2}{3}\frac{1}{3}\bar{u}$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-u$ with $u=0.022$
 3 Al: $\frac{3}{4}$ of positions of (f) with $u'=0.178$, 3 Al: same with $u''=-0.178$
 12 Al: (k) $u\bar{v}$; etc. (see 1930, 352, p. 169) with $u=\frac{1}{6}, v=-0.106$
 12 O: (k) $u_1\bar{u}_1v_1$; etc. with $u_1=\frac{1}{6}, v_1=0.05$
 12 O: (k) $u_2\bar{u}_2v_2$; etc. with $u_2=\frac{1}{2}, v_2=0.144$
 4 O: (f) $\frac{1}{3}\frac{2}{3}u_3$; etc. with $u_3=-0.05$
 4 O: (e) $00w$; $00\bar{w}$; $0, 0, \frac{1}{2}-w$; $0, 0, w+\frac{1}{2}$ with $w=0.144$
 $\frac{3}{2}$ O: $1\frac{1}{2}$ of two equivalent positions (c) $\frac{1}{3}\frac{2}{3}\frac{1}{4}$; $\frac{2}{3}\frac{1}{3}\frac{3}{4}$,
 $\frac{3}{2}$ O: same for (d) $\frac{1}{3}\frac{2}{3}\frac{3}{4}$; $\frac{2}{3}\frac{1}{3}\frac{1}{4}$.

This distribution of atoms among the equivalent positions of the space group is so bizarre that a confirmation of the structure is much to be desired.

(n) The atomic arrangement in $\gamma\text{-Al}_2\text{O}_3$ has not yet been satisfactorily established.

TABLE I. PARAMETERS ASSIGNED TO THE ATOMS IN Sb_2S_3

Atom	u	v
Sb(1)	0.328	0.031
Sb(2)	-.039	-.149
S(1)	.883	.047
S(2)	-.439	-.125
S(3)	.194	.208

(o) Spectral photographs of stibnite indicate that the four Sb_2S_3 molecules in its orthorhombic unit are arranged according to V_h^{16} . All atoms are said to be in special positions (c) $uv\frac{1}{4}$; $\bar{u}\bar{v}\frac{3}{4}$; $\frac{1}{2}-u, v+\frac{1}{2}, \frac{1}{4}$; $u+\frac{1}{2}, \frac{1}{2}-v, \frac{3}{4}$ with the parameters of Table I. If abc are the axes of this description and $X'Y'Z'$ are those of 1930, 352: $a=Z'$, $b=Y'$, $c=X'$, the origin being moved to a center of symmetry. Within the limit of experimental error the Bi parameters in Bi_2S_3 are the same as those of Sb.

This structure consists of chains of the composition $(Sb_2S_3)_n$. If the atoms have their uncharged radii, there is good contact within these chains (Figure 287). Whether the atoms are charged or neutral the atoms in adjacent chains are unexpectedly far apart. In view of this fact it will be important to see whether future work confirms this arrangement.

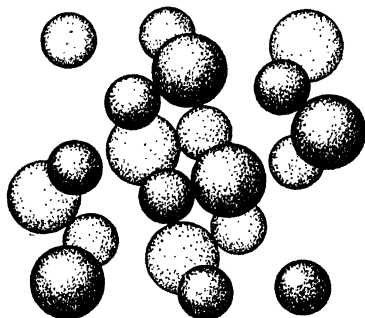
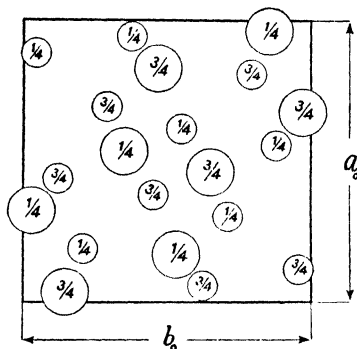


FIG. 287a.—(left) The arrangement proposed for stibnite, Sb_2S_3 , projected on its c -face. The large circles are Sb atoms.

FIG. 287b.—(right) A packing drawing of a if Sb and S are given their neutral radii. The small spheres thus are the sulfur atoms. Packing is not improved by assuming that the atoms are charged.

(*p*) A reexamination of Mg_3P_2 shows that its correct structure is identical with that of Tl_2O_3 (*b*). The selected parameters are the same as those found for bixbyite, $(Fe, Mn)_2O_3$. This atomic arrangement also prevails for Be_3P_2 , Be_3N_2 , Mg_3N_2 and α - Ca_3N_2 .

It is said that Zn_3P_2 , Cd_3P_2 and Zn_3As_2 , though likewise possessed of 16-molecule cubic units, have different structures.

The earlier choice of a 12-molecule cube for Mg_3N_2 was due to a faulty estimate of its density.

Probably the small unit previously determined for Cd_3As_2 is equally wrong.

(*q*) The monoclinic unit assigned to Cd_3Sb_2 contains four molecules.

(*r*) The structure first suggested for the magnetic γ - Fe_2O_3 was the same as that of magnetite [(*k*) of Chapter XVI] with four oxygen atoms added. It has recently been shown that if these additional atoms are put in either of the two sets of positions originally proposed, the observed intensities cannot be explained. Better intensity agreement can be obtained by placing these atoms in (4g) uuu ; etc. with $u = \frac{1}{8}$. The smallest O-O separations in this structure are greater than those existing in the previous arrangements; nevertheless they still have the improbably small value 2.14 Å.

(*s*) Eight molecules of Fe_3W_2 are contained in the large cell found for the ϵ -phase of the Fe-W system.

TABLE II. THE CRYSTAL STRUCTURES OF THE COMPOUNDS R_2X_3

Substance, symmetry and structure type		a_o	c_o or α	References
Al_2Mg_3	Cubic (t)	10.54		1934, 340.
$\alpha-Al_2O_3$	Hexagonal Fe_2O_3 (a)	5.13	55°6'	1930, 246b.
$\beta-Al_2O_3$	Hexagonal (f), (m)	5.56	22.55	1931, 56.
$\gamma-Al_2O_3$	Cubic (n)	7.90		1932, 18, 75.
As_2O_3	Cubic As_2O_3 (e)	11.0457± 0.0002		1932, 290.
Be_3N_2	Cubic Tl_2O_3 (b), (p)	8.134		1933, 443.
Be_3P_2	Cubic Tl_2O_3 (b), (p)	10.15		1933, 443.
Bi_2S_3 (Bismuthinite)	Ortho- rhombic Sb_2S_3 (k), (o)	11.13	3.97 $b_o = 11.27$	1933, 207.
$\alpha-Ca_3N_2$	Cubic Tl_2O_3 (b), (p)	11.40		1933, 137, 443.
Cd_3As_2	Cubic (p)	12.58 (?)		
Cd_3P_2	Cubic (p)	12.26		1933, 443.
Cd_3Sb_2	Monoclinic (q)	7.20	6.16 $b_o = 13.51, \beta = 100^\circ 14'$	1933, 167.
Cr_3C_2	Ortho- rhombic (g)			1931, 468.
Cr_2O_3	Hexagonal Fe_2O_3 (a)	5.38	54°50'	1930, 246b.
Fe_2O_3 (Hematite)	Hexagonal Fe_2O_3 (a)	5.4135	55°17'	1930, 246b; 1932, 75; 1933, 247; 1934, 34.
Fe_2O_3 (Magnetic)	Cubic (h), (r)			1931, 117, 445.
Fe_3W_2 (ϵ -phase)	Hexagonal (s)	4.738	25.726	1931, 343.
Mg_3As_2	Cubic Tl_2O_3 (b), (p)	12.33		1933, 443, 524.
Mg_3Bi_2	Hexagonal La_2O_3 (c)	4.666	7.401	1933, 524.
Mg_3N_2	Cubic Tl_2O_3 (b), (i), (p)	9.95		1932, 185; 1933, 443.
Mg_3P_2	Cubic Tl_2O_3 (b), (p)	12.03		1933, 443, 524.
Mg_3Sb_2	Hexagonal* La_2O_3 (c)	4.573	7.229	1933, 524.
Sb_2S_3 (Stibnite)	Ortho- rhombic Sb_2S_3 (k), (o)	11.20	3.83 $b_o = 11.28$	1933, 207.
Zn_3As_2	Cubic (p)	11.74		1933, 443.
Zn_3P_2	Cubic (p)	11.42		1933, 443.

* The parameters are the same as those of La_2O_3 .

(t) The intermetallic phase Al_2Mg_3 gives the cubic pattern of α -Mn. It is therefore concluded that the true composition is $Mg_{17}Al_{12}$ with two molecules per cell. In such a structure Mg atoms presumably are in (2a), (8a) and (24g) (book, p. 270) with $u=0.356$, $v=0.042$; the Al atoms, also in (24g), have $u'=0.089$, $v'=0.278$.

Chapter XIVA. Structures of the Type RX_3 , of Higher Compounds R_mX_n and of New Compounds of the Type $R_x(MX_2)_y$

The Compounds R_mX_n

(al) AlF_3 was earlier described as hexagonal with a unit containing three molecules. An atomic arrangement more recently found for it is rhombohedral with two molecules in the unit (corresponding to a six-molecule hexagonal cell). The structure, based on D_3^7 , has atoms in the special positions:

$$\begin{aligned} Al: & \text{ (c) } uuu; \bar{u}\bar{u}\bar{u} \text{ with } u=0.237 \\ F: & \text{ (d) } u_1\bar{u}_10; \bar{u}_10u_1; 0u_1\bar{u}_1 \text{ with } u_1=0.430 \\ & \text{ (e) } u'\bar{u}'\frac{1}{2}; \bar{u}'\frac{1}{2}u'; \frac{1}{2}u'\bar{u}' \text{ with } u'=0.070. \end{aligned}$$

(am) **Arsine, AsH_3 , and phosphine, PH_3 ,** when solidified give patterns corresponding to four-molecule cubic cells. They are said to be face-centered but a further study of them is desirable to be sure that they do not have structures like ammonia (*l*).

(an) A previous determination has given AsI_3 , SbI_3 and BiI_3 hexagonal unit cells containing six molecules. Atomic positions, said to be developed from C_3^1 , were stated for BiI_3 [see (*b*)]. More recent work on AsI_3 has shown that its space group really is C_{3i}^2 . The atoms in the two-molecule rhombohedron that is its true unit have the coordinates:

$$\begin{aligned} As: & \text{ (c) } \pm(uuu) \text{ with } u=\frac{1}{6} \\ I: & \text{ (f) } \pm(xyz); \pm(zxy); \pm(yzx) \text{ with } x=0.42, y=0.08, z=0.75. \end{aligned}$$

If, as is presumably the case, SbI_3 and BiI_3 are isomorphous with AsI_3 , then their two-molecule rhombohedral units will have the dimensions of Table I.

Though the space groups and the unit cell suggested for $CrBr_3$ are hexagonal, it is reported to be isomorphous with BiI_3 . Its true unit is thus without doubt rhombohedral, the dimensions being those stated in Table I.

TABLE I. THE CRYSTAL STRUCTURES OF THE COMPOUNDS R_mX_n

Substance, symmetry and structure type		a_o	c_o or α		References
Compounds RX_3					
AlF_3	Hexagonal	(<i>i</i>), (<i>al</i>)	5.029	58°31'	1931, 256; 1933, 255.
Al_2Fe	Ortho- rhombic	(<i>bs</i>)	11.87 (?)	15.80 $b_o=8.09$	1933, 334; 1934, 313, 313a.
AsH_3	Cubic	(<i>am</i>)	6.40 at -170° C		1930, 429.
AsI_3	Hexagonal	AsI_3 (<i>b</i>), (<i>an</i>)	8.25	51°20'	1931, 205, 206.
BiI_3	Hexagonal	AsI_3 (<i>b</i>), (<i>an</i>)	8.13	54°50'	
$CaPb_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.891		1933, 529.
$CaSn_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.732		1933, 529.
$CaTl_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.794		1933, 529.
(Ce, La, . . .)F ₃ (Tysonite)	Hexagonal	(<i>ap</i>)			1931, 335.
$CeMg_3$	Cubic	$LaMg_3$ (<i>bc</i>)	7.373		1934, 234.
$CePb_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.864		1933, 529.
$CeSn_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.711		1933, 529.
CoF_3	Hexagonal	(<i>aq</i>)	3.66 ₄	87°20'	1931, 100.
$CrBr_3$	Hexagonal	AsI_3 (<i>b</i>), (<i>an</i>)	7.05	52°36'	1932, 68.
CrO_3	Ortho- rhombic (?)	(<i>as</i>)	8.50	5.72 $b_o=4.73$	1931, 53, 487.
Fe_3C	Ortho- rhombic	(<i>o</i>), (<i>av</i>)	4.626	6.633 $b_o=5.107$	1931, 343; 1932, 474.
$FeCl_3$	Hexagonal	AlF_3 (?) (<i>al</i>)	6.69	52°30'	1932, 481.
FeF_3	Hexagonal	(<i>aq</i>)	3.75 ₆	88°14'	1931, 100, 256; 1933, 511.
KCNS	Ortho- rhombic	(<i>aw</i>)	6.66	6.635 $b_o=7.58$	1933, 261; 1934, 38.
$LaMg_3$	Cubic	$LaMg_3$ (<i>bc</i>)	7.478		1934, 234.
$LaPb_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.893		1933, 386.
$LaSn_3$	Cubic	$AuCu_3$ (<i>e</i>), (<i>ao</i>)	4.772		1933, 386.
$LiCd_3$		(<i>at</i>)			1933, 27; 1934, 310.
MoO_3	Ortho- rhombic	(<i>ax</i>)	3.954	3.694 $b_o=13.825$	1931, 53, 484, 485.
NH_3	Cubic	(<i>t</i>)	5.08 at -170° C		1930, 429.
$NaCN O$	Hexagonal	$CsCl_2I$ (<i>d</i>)	5.45	38°16'	1934, 287.
NaN_3	Hexagonal	$CsCl_2I$ (<i>d</i>), (<i>ar</i>)	5.45	38°48'	1934, 287.

Substance, symmetry and structure type			a_o	c_o or α	References
NaPb ₃	Cubic	AuCu ₃ (<i>e</i>), (<i>ao</i>)	4.873		1931, 505.
PH ₃	Cubic	(<i>am</i>)	6.31 at	-170° C	1930, 429.
PI ₃	Hexagonal	(<i>ay</i>)	7.11	7.42	1933, 64.
PdF ₃	Hexagonal	(<i>aq</i>)	3.75 ₃	84°29'	1931, 100.
PrMg ₃	Cubic	LaMg ₃ (<i>bc</i>)	7.373		1934, 234.
RbN ₃	Tetragonal	KN ₃ (<i>c</i>)			1931, 72.
RcO ₃	Cubic	(<i>az</i>)	3.734		1931, 44; 1932, 308; 1933, 45.
RhF ₃	Hexagonal	(<i>aq</i>)	3.62	84°48'	1931, 100.
SbI ₃	Hexagonal	AsI ₃ (<i>b</i>), (<i>an</i>)	8.18	54°14'	
SrPb ₃	Tetragonal	(<i>ba</i>)	4.955	5.025	1933, 529.
TiAl ₃	Tetragonal	(<i>au</i>)	5.424	8.574	1931, 114.
TiCN ₃	Ortho- rhombic	(<i>aw</i>)	6.80	6.78	1934, 38, 256.
WO ₃	Triclinic	(<i>bb</i>)	7.28	$b_o=7.52$ $b_o=7.48^*$	1931, 53.

Compounds RX_4

Cl ₄	Cubic	(<i>bd</i>)	9.14		1931, 164.
Cr ₄ C	Cubic	(<i>x</i>)			1931, 468.
Fe(CO) ₄	Monoclinic	(<i>be</i>)	13.00	11.41	1931, 62.
			$b_o=11.41$, $\beta=85^\circ35'$		
HfF ₄	Monoclinic	(<i>bt</i>)	9.45	7.62	1934, 240a.
			$b_o=9.84$, $\beta=94^\circ29'$		
LaAl ₄	Tetragonal	(<i>bf</i>)	13.2	10.2	1933, 385.
SiF ₄	Cubic	(<i>bg</i>)			1930, 218a.
SiI ₄	Cubic	SnI ₄ (<i>aa</i>)	11.986		1931, 163.
TiBr ₄	Cubic	SnI ₄ (<i>aa</i>)	11.250		1932, 194.
TiI ₄	Cubic	SnI ₄ (<i>aa</i>)	12.002		1932, 194.
ZrF ₄	Monoclinic	(<i>bt</i>)	9.46	7.64	1934, 240a.
			$b_o=9.87$, $\beta=94^\circ30'$		

Compounds RX_5

MgZn ₅	Hexagonal	(<i>bh</i>)	9.92	16.48	1933, 465.
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Compounds RX_6

BaB ₆	Cubic	ThB ₆ (<i>ac</i>), (<i>bj</i>)	4.28		1931, 425; 1932, 6, 428.
B ₂ C (?)	Hexagonal	(<i>bu</i>)	5.62	12.12	1934, 338.
CaB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.145		1931, 425; 1932, 6, 428; 1934, 207.
CeB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.129		1931, 425; 1932, 6, 428.
ErB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.102		1932, 6, 428.
GdB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.12		1932, 6.
LaB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.145		1931, 425; 1932, 6, 428.

* All angles close to 90°.

Substance, symmetry and structure type			a_o	c_o or α	References
NdB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.118		1932, 6, 428.
PrB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.121		1932, 428.
SrB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.19		1931, 425; 1932, 6, 428.
Te(OH) ₆	Cubic	(<i>ab</i>), (<i>bi</i>)			1934, 88.
Te(OH) ₆ (second form)	Monoclinic	(<i>bi</i>)	5.54	9.74	1934, 88.
			$b_o=9.30, \beta=104^\circ 30'$		
ThB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.15		1932, 6.
YB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.07		1932, 6.
YtB ₆	Cubic	ThB ₆ (<i>bj</i>)	4.13		1932, 6.

Higher Compounds RX_n

CsC ₈	Hexagonal	KC ₈ (<i>bk</i>)	4.94	23.76	1932, 405.
KC ₈	Hexagonal	KC ₈ (<i>bk</i>)	4.94	21.34	1932, 405.
RbC ₈	Hexagonal	KC ₈ (<i>bk</i>)	4.94	22.73	1932, 405.
CsC ₁₆	Hexagonal	KC ₁₆ (<i>bl</i>)	4.94	18.51	1932, 405.
KC ₁₆	Hexagonal	KC ₁₆ (<i>bl</i>)	4.94	17.45	1932, 405.
RbC ₁₆	Hexagonal	KC ₁₆ (<i>bl</i>)	4.94	17.95	1932, 405.

Miscellaneous Compounds R_mX_n

Ag ₃ Hg ₄	Cubic	(<i>bn</i>)	10.09		1933, 494.
Al ₄ C ₃	Hexagonal	(<i>bv</i>)	8.53	22°28'	1934, 354c.
B ₁₀ H ₁₄	Ortho- rhombic	(<i>bo</i>)	14.46	5.69	1931, 304.
			$b_o=20.85$		
Co ₄ S ₃	Cubic		9.91		1932, 90.
Cr ₇ C ₃	Hexagonal	(<i>af</i>)	13.98	4.52	1931, 468.
Cu ₅ Cd ₈	Cubic	Cu ₅ Zn ₈ (<i>ad</i>)			1931, 51.
Cu ₁₅ Si ₄	Cubic	(<i>bg</i>)	9.694		1934, 179.
Cu ₅ Zn ₈	Cubic	Cu ₅ Zn ₈ (<i>ad</i>)			1931, 51.
Na ₃₁ Pb ₈	Cubic	(<i>bp</i>)	13.27		1933, 451.
Sb ₂ Tl ₇	Cubic	(<i>bm</i>)	11.59		1934, 180.
W ₄ O ₁₁	Tetragonal	(<i>br</i>)	7.56	3.735	1934, 74.

TABLE II. NEW CRYSTAL STRUCTURES OF THE COMPOUNDS R_x(MX₂)_y

Substance, symmetry and structure type			a_o	c_o or α	References
AgClO ₂	Pseudo- tetragonal	(<i>ca</i>)	12.17	6.69	1931, 282.
AgSbS ₂ (Miargyrite)	Monoclinic	(<i>cb</i>)	13.17	12.82	1932, 219.
			$b_o=4.39, \beta=98^\circ 37\frac{1}{2}'$		
(Ag, Cu) ₂ Sb ₂ S ₄ (Polybasite)	Ortho- rhombic (?)	(<i>cc</i>)	7.50	11.95	1934, 89.
			$b_o=12.99$		
CaB ₂ O ₄	Ortho- rhombic	(<i>cd</i>)	6.19	4.28	1931, 494; 1932, 494.
			$b_o=11.60$		
Ca(ClO ₂) ₂	Pseudo- cubic	(<i>ce</i>)	5.80		1931, 282.
CuBiS ₂ (Emplectite)	Ortho- rhombic	(<i>cf</i>)	6.12	14.51	1932, 219; 1933, 206.
			$b_o=3.89$		

Substance, symmetry and structure type			a_o	c_o or α	References
$Cu_2Fe_2O_4$	Hexagonal		6.06	2.82	1934, 281.
$CuFeS_2$ (Chalcopyrite)	Tetragonal	[XI, (aa)], (cg)	5.24	10.30	1932, 359.
$CuSbS_2$ (Wolfsbergite)	Ortho- rhombic	(cf)	6.01	14.46 $b_o=3.78$	1932, 219; 1933, 206.
$KAg(CN)_2$	Hexagonal	(ch)	7.384	17.55	1933, 199.
$K_2Fe_2O_4$	Cubic	(ci)	7.958		1933, 197.
$KFeS_2$	Hexagonal	(cj)	13.03	5.40	1933, 329.
$Li_2Fe_2O_4$	Cubic	(ck)	4.141		1931, 362.
NH_4ClO_2	Tetragonal	(cl)	6.30	3.73	1931, 282.
NH_4HF_2	Ortho- rhombic	(cm)	8.33	3.68 $b_o=8.14$	1932, 196; 1933, 349.
$NH_4H_2PO_2$	Ortho- rhombic	(cr)	3.98	11.47 $b_o=7.57$	1934, 307.
$Na_2Fe_2O_4$	Hexagonal	(cn)	5.59	$35^\circ 20'$	1933, 149.
$NaNNO_2$	Ortho- rhombic	(co)	3.55	5.37 $b_o=5.56$	1931, 504.
$Pb(ClO_2)_2$	Pseudo- tetragonal	(cp)	4.14	6.25	1931, 282.
$PbFe_2O_4$	Cubic		7.81		1933, 197.
$TlAsS_2$ (Lorandite)	Monoclinic	(cq)	15.02	6.10 $b_o=11.31, \beta=127^\circ 45'$	1932, 219.

(ao) Several intermetallic compounds, of which $NaPb_3$ is typical, have been found to have the simple cubic arrangement (e) which occurs as a superlattice in alloys of copper with gold, platinum and palladium. For $NaPb_3$ the atomic coordinates are: Na: (1a) 000, Pb: (3a) $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$ (Figure 288a and b).

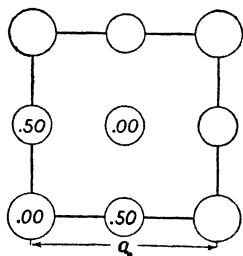
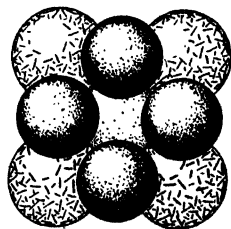


FIG. 288a.—(left) A cube face projection of the simple $NaPb_3$ grouping. Na atoms are at the origin.

FIG. 288b.—(right) A packing drawing of a with the atoms having the (neutral) radii found in the metals themselves. Na atoms are line-shaded.



(ap) A new structure has been suggested for tysonite (Ce, La, \dots) $F_3 = R'F_3$. It has atoms of its six-molecule unit in the following special positions of D_{6h}^3 :

R: (g) $uu0$; etc. (1930, 352, p. 168) with $u=ca$ 0.34

F: (a) 000 ; $00\frac{1}{2}$, at (c) $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}\frac{1}{2}$; $\frac{2}{3}\frac{1}{3}0$; $\frac{1}{3}\frac{2}{3}\frac{1}{2}$ and at (k) $u'u'v$; etc. with $u'=ca$ $\frac{2}{3}$ and $v=ca$ 0.175.

This arrangement is not definitely established by the existing data.

(aq) The data on FeF_3 are conflicting. According to 1931, 256 it is hexagonal with a three-molecule unit. The analysis of 1931, 100 gives it a one-molecule rhombohedron having the dimensions recorded in Table I. A recent discussion suggests that neither of these is correct but that the arrangement really resembles that of WO_3 (bb). Whatever structure may ultimately be established for FeF_3 , it probably is possessed by CoF_3 , RhF_3 and PdF_3 as well. The one-molecule rhombohedral units, or pseudo-units, of these substances are listed in Table I.

(ar) The cell dimensions of NaN_3 have been determined at 200°C as well as at room temperature. At the higher temperature the edge length is unchanged, $a_0 = 5.45 \text{ \AA}$; the rhombohedral angle, however, has become slightly less acute, $\alpha = 39^\circ 14'$. The parameter u for nitrogen has not been established for any of the sodium compounds showing this arrangement; for CsCl_2I it was 0.31.

(as) The unit cell of CrO_3 contains four molecules. A structure based on V_h^{17} has been suggested but not proved.

(at) The data on LiCd_3 are conflicting. According to one investigator it is cubic with a cell apparently holding 6 molecules; others state that the arrangement is hexagonal close-packed.

(au) The tetragonal unit of TiAl_3 contains four molecules. An atomic arrangement has been described which, based on V_d^8 , has atoms in the following special positions:

$$\begin{array}{ll} \text{Ti:} & \text{(a) } 000; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2} \\ & \text{Al(1): (b) } \frac{1}{2}\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}0; 00\frac{1}{2}; \frac{1}{2}00 \\ \text{Al(2): (c) } & \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4} \\ & \text{Al(3): (d) } \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}. \end{array}$$

(av) It has been found that the agreement between observed and calculated intensities from Fe_3C can be improved by altering very slightly the parameters of the iron atoms and by placing the carbon atoms in positions different from those previously suggested. As before, the iron atoms are in the following special positions of V_h^{16} :

$$\text{Fe: (c) } uv\frac{1}{4}; \text{ etc. (see p. 266 of book) with } u=0.833, v=0.04$$

$$\text{Fe: (d) } xyz; \text{ etc. with } x=0.333, y=0.175, z=0.065.$$

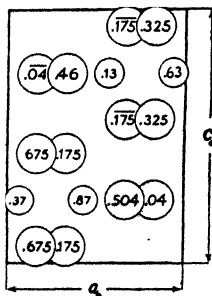
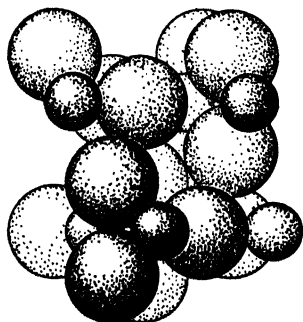


FIG. 289a.—(left) The improved structure for Fe_3C projected on the b-face of its orthorhombic cell. The large circles are the iron atoms.

FIG. 289b.—(right) A packing drawing of Fe_3C if the (larger) Fe atoms have their neutral (metallic) radii and the C atoms have the radius suggested by the diamond.



Instead of being in symmetry centers the carbon atoms are in another set of (c) $u'v'\frac{1}{4}$ with $u'=0.43$, $v'=0.87$. The resulting interatomic distances give iron the radius found in the metal, 1.25 Å; the radius of carbon, 0.76 Å, is that which occurs in the diamond (Figure 289a and b).

(aw) The orthorhombic unit of **KCNS** contains four molecules. A structure which gives fairly good agreement between calculated and photographically observed intensities is obtained by putting atoms in the following special positions of V_h^{11} :

$$\begin{aligned} \text{K: (c) } & u'0\frac{3}{4}; \bar{u}'\frac{1}{2}\frac{1}{4}; \bar{u}'0\frac{1}{4}; u'\frac{1}{2}\frac{3}{4} \text{ with } u'=0.212 \\ \text{N, C, S: (d) } & u\frac{1}{4}v; \bar{u}\frac{3}{4}\bar{v}; \bar{u}, \frac{1}{4}, v+\frac{1}{2}; u, \frac{3}{4}, \frac{1}{2}-v \text{ with} \\ & u(\text{S})=0.400, v(\text{S})=0.095. \end{aligned}$$

The suggested parameters for nitrogen are $u(\text{N})=0.080$, $v(\text{N})=0.400$; for carbon $u(\text{C})=0.205$, $v(\text{C})=0.280$. To derive the axes of this description (abc) from those of 1930, 352 ($X'Y'Z'$) the transformations $a=Z'$, $b=X'$, $c=Y'$ are necessary. The kind of packing provided by this arrangement is illustrated by Figure 290.

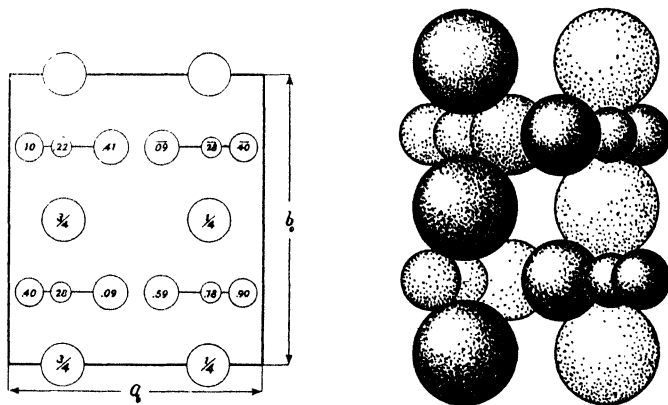


FIG. 290a.—(left) The structure assigned to KCNS as projected upon the c -face of its orthorhombic unit. The largest circles are K atoms; the others, in order of decreasing size, are S, N, and C.

FIG. 290b.—(right) A packing drawing of a . In this figure K atoms have their ionic size but for lack of better knowledge the other atoms have been assigned their neutral radii.

The thallium salt, **TICNS**, probably has the same atomic grouping as **KCNS**. In fact one of the two studies (1934, 38) of **TICNS** makes it orthorhombic with a similarly shaped unit and the same space group V_h^{11} . Another determination, which presumably is wrong, found it to be tetragonal with a unimolecular cell.

(ax) The orthorhombic unit of **MoO₃** contains four molecules. Two determinations agree in placing the molybdenum atoms in special positions (c) of V_h^{11} : $uv\frac{1}{4}$; etc. (see p. 266 of book). The parameters found for

these atoms are practically identical: $u=0.086$ (0.088), $v=0.099$ (0.101). According to one study (1931, 484, 485) the oxygen atoms likewise are in three sets of these special positions (c) with $u_1=0.086$, $v_1=0.25$, $u_2=0.586$, $v_2=0.099$, $u_3=0.086$, $v_3=0.070$.

(ay) The unit cell of PI_3 contains two molecules. It is said that the space group is C_6^6 with a structure similar to that of iodoform, CHI_3 [see p. 372 (z) of book]. The parameters chosen for the iodine atoms are $x=0.30$, $y=0.35$; z presumably being zero.

(az) No evidence has been obtained that the unit cube of ReO_3 is larger than the one-molecule cell of the table. The Re atom is at the origin 000; it is thought that the three oxygen atoms are at (3b) $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$. This arrangement is said to resemble that of WO_3 which according to (bb) is triclinic.

(ba) The structure assigned to SrPb_3 is a slight distortion of the NaPb_3 grouping (ao). The tetragonal unit contains one molecule with atoms in the following special positions: Sr: 000, Pb: $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

(bb) The cell of WO_3 listed in the table contains four molecules. The following atomic arrangement, based on C_1^1 , has been reported for its atoms:

W: (i) xyz ; $\bar{x}\bar{y}\bar{z}$ with $x'=\frac{1}{4}$, $y'=\frac{1}{3\frac{1}{2}}$, $z'=\frac{1}{1\frac{1}{6}}$, and $x''=\frac{1}{4}$, $y''=\frac{1}{3\frac{1}{2}}$, $z''=-\frac{1}{1\frac{1}{6}}$
 O: (a) 000, (d) $\frac{1}{2}00$, (c) $0\frac{1}{2}0$, (e) $\frac{1}{2}\frac{1}{2}0$,
 (i) xyz ; $\bar{x}\bar{y}\bar{z}$ with $x_1=\frac{1}{4}$, $y_1=\frac{9}{3\frac{1}{2}}$, $z_1=0$; $x_2=\frac{1}{4}$, $y_2=-\frac{7}{3\frac{1}{2}}$, $z_2=0$; $x_3=\frac{1}{4}$,
 $y_3=\frac{1}{3\frac{1}{2}}$, $z_3=\frac{9}{1\frac{1}{6}}$; $x_4=\frac{1}{4}$, $y_4=\frac{1}{3\frac{1}{2}}$, $z_4=\frac{7}{1\frac{1}{6}}$.

A more thorough study of WO_3 is obviously needed; whether this arrangement is correct or not, the unit described above is undoubtedly not the simplest one possible.

(bc) The cubic arrangement found for LaMg_3 and several intermetallic compounds like it has four molecules in the special positions:

La: (4b) 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$
 Mg: (4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$
 Mg: (4d) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$
 Mg: (4e) $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

(bd) A new study of Cl_4 found diffraction lines incompatible with an SnI_4 -like grouping. It is said that this new pattern corresponds to a four-molecule unit cube but no structure has been deduced.

(be) The large monoclinic cell of $\text{Fe}(\text{CO})_4$ described in the table is said to be built upon C_{2h}^6 and to contain 12 molecules. Making the doubtful assumption that this is the true unit it is concluded that the molecule of iron carbonyl is $[\text{Fe}(\text{CO})_4]_3$.

(bf) The tetragonal cell of LaAl_4 is thought to contain 16 molecules.

(bg) An analysis which is undoubtedly wrong makes SiF_4 , solidified at -170°C , cubic with a two-molecule unit having $a_0 = 5.41 \text{ \AA}$. Faulty interatomic distances prevail in the suggested arrangement.

(bh) The unit chosen for MgZn_5 is said to contain 16 molecules. A structure derived from that given to MgZn has been discussed.

(bi) A recent study of telluric acid, $\text{Te}(\text{OH})_6$, contains evidence which is thought to show that the unit of its cubic modification is not the large 32-molecule cell previously found. This new cube contains four molecules and has half the edge length, $a_0 = 7.83 \text{ \AA}$.

Four molecules are also to be found in the monoclinic unit of the second form of $\text{Te}(\text{OH})_6$; the space group is reported to be C_{2h}^5 .

(bj) The unit cube of the ThB_6 arrangement contains a single molecule and is based on O_h^1 . Placing the metal atom at the origin 000, the boron atoms form an octahedron with the coordinates (Figure 291a):

$$\text{B: (6d) } \frac{1}{2}u; \frac{1}{2}u\frac{1}{2}; u\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\bar{u}; \frac{1}{2}\bar{u}\frac{1}{2}; \bar{u}\frac{1}{2}\frac{1}{2}.$$

In CaB_6 , which has been studied more fully than the other compounds of this type, $u = 0.207$ giving a B-B separation of 1.716 \AA . In Figure 291b where the origin has been translated to a B_6 center at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the structure appears as a body-centered CsCl packing of metal atoms and boron octahedra.

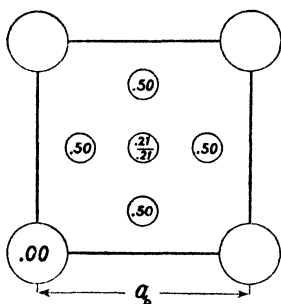
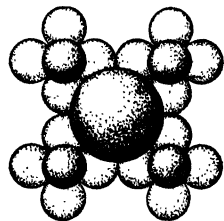


FIG. 291a.—(left) The unit of the CaB_6 grouping projected on a cube face. Small circles are B atoms.

FIG. 291b.—(right) A packing drawing of CaB_6 giving the atoms their neutral radii. The calcium atom at the origin of a has been translated to the cube center of this drawing.



(bk) The **brown alkali graphites** have been given the composition RC_8 . Their four-molecule hexagonal cells have $a_0 = 4.94 \text{ \AA}$, twice that of graphite. The alkali atoms are between the graphite layers in positions which have not been exactly fixed.

(bl) The **black alkali graphites** are said to be RC_{16} . Their units containing two molecules also have bases with twice the edge length and four times the area of graphite. It is considered that they are derived from the brown graphites by allowing alternate layers of alkali atoms to distill away.

(bm) Crystals of the intermetallic compound Sb_2Tl_7 provide an example of a body-centered cubic superlattice. Atomic positions in the

four-molecule cube, as determined from photographic data, are the following special positions of O_h^9 (1930, 352, p. 148):

12 Sb: (12a) $\pm(u00)$; $\pm(0u0)$; $\pm(00u)$ and 6 similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, with $u=0.29$

2 Tl: (2a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

16 Tl: (16d) $\pm(u'u'u')$; $\pm(u'\bar{u}'\bar{u}')$; $\pm(\bar{u}'u'\bar{u}')$; $\pm(\bar{u}'\bar{u}'u')$ and 8 similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ with $u'=0.167$

24 Tl: (24j) $\pm(u_1u_10)$; $\pm(u_1\bar{u}_10)$; $\pm(0u_1u_1)$; $\pm(0u_1\bar{u}_1)$; $\pm(u_10u_1)$; $\pm(\bar{u}_10u_1)$ and 12 similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ with $u_1=0.35$.

(bn) The atomic arrangement given to Ag_3Hg_4 has a four-molecule unit cube with atoms in the following special positions of O_h^9 :

Ag: (12h) $\frac{1}{2}0\frac{1}{4}$; $\frac{1}{2}0\frac{3}{4}$; $\frac{1}{4}\frac{1}{2}0$; $\frac{3}{4}\frac{1}{2}0$; $0\frac{1}{4}\frac{1}{2}$; $0\frac{3}{4}\frac{1}{2}$ and 6 similar coordinates about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

Hg: (16d) uuu ; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$; $\bar{u}uu$; $u\bar{u}u$; $uu\bar{u}$ and 8 similar coordinates about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ with $u=0.192$.

(bo) The orthorhombic unit assigned to $B_{10}H_{14}$ would contain eight molecules; its space group is said to be V_h^{21} .

(bp) The so-called Na_4Pb phase of the Na-Pb system has been said to be actually $Na_{31}Pb_8$ with a cubic structure like that of $Cu_{31}Sn_8$ (ad).

(bq) The complete structure found for the cubic intermetallic compound $Cu_{15}Si_4$ is developed from T_d^6 . Silicon atoms in its four-molecule cell are in (1930, 352, p. 131):

(16f) uuu ; $u, \bar{u}, \frac{1}{2}-u$; $\frac{1}{2}-u, u, \bar{u}$; $\bar{u}, \frac{1}{2}-u, u$; $u+\frac{1}{4}, u+\frac{1}{4}, u+\frac{1}{4}$;
 $\frac{1}{4}-u, u+\frac{1}{4}, \frac{3}{4}-u$; $u+\frac{1}{4}, \frac{3}{4}-u, \frac{1}{4}-u$; $\frac{3}{4}-u, \frac{1}{4}-u, u+\frac{1}{4}$

and similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, with $u=0.208$. Copper atoms are in:

(12k) $\frac{3}{8}0\frac{1}{4}$; $\frac{1}{8}0\frac{3}{4}$; $\frac{1}{4}\frac{3}{8}0$; $\frac{3}{4}\frac{1}{8}0$; $0\frac{1}{4}\frac{3}{8}$; $0\frac{3}{4}\frac{1}{8}$ and similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

and in

(e) xyz ; $x, \bar{y}, \frac{1}{2}-z$; $\frac{1}{2}-x, y, \bar{z}$; $\bar{x}, \frac{1}{2}-y, z$;
 zxy ; $\frac{1}{2}-z, x, \bar{y}$; $\bar{z}, \frac{1}{2}-x, y$; $z, \bar{x}, \frac{1}{2}-y$;
 yzx ; $\bar{y}, \frac{1}{2}-z, x$; $y, \bar{z}, \frac{1}{2}-x$; $\frac{1}{2}-y, z, \bar{x}$;
 $y+\frac{1}{4}, x+\frac{1}{4}, z+\frac{1}{4}$; $\frac{1}{4}-y, x+\frac{1}{4}, \frac{3}{4}-z$; $y+\frac{1}{4}, \frac{3}{4}-x, \frac{1}{4}-z$; $\frac{3}{4}-y, \frac{1}{4}-x, z+\frac{1}{4}$;
 $x+\frac{1}{4}, z+\frac{1}{4}, y+\frac{1}{4}$; $x+\frac{1}{4}, \frac{3}{4}-z, \frac{1}{4}-y$; $\frac{3}{4}-x, \frac{1}{4}-z, y+\frac{1}{4}$; $\frac{1}{4}-x, z+\frac{1}{4}, \frac{3}{4}-y$;
 $z+\frac{1}{4}, y+\frac{1}{4}, x+\frac{1}{4}$; $\frac{3}{4}-z, \frac{1}{4}-y, x+\frac{1}{4}$; $\frac{1}{4}-z, y+\frac{1}{4}, \frac{3}{4}-x$; $z+\frac{1}{4}, \frac{3}{4}-y, \frac{1}{4}-x$

and similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ with $x=0.12$, $y=0.16$, $z=-0.04$.

(br) A tetragonal tungsten oxide, of the apparent composition W_4O_{11} , has been found to have a unit of almost the same size and shape as the triclinic unit assigned to WO_3 . One W_4O_{11} molecule is contained in this cell and it is thought that its atomic arrangement is practically the same as that of WO_3 with one oxygen atom per cell removed.

(bs) The unit prism of Al_3Fe (Table I) is said to contain 24 molecules. A recent study makes a_0 four times as big (47.43 Å) with V_h^{23} as space group. Such a cell is reported to have in it 400 atoms.

(bt) The large cells of HfF_4 and ZrF_4 of Table I would enclose 12 molecules. The space group is C_{2h}^6 .

(bu) If boron carbide is B_6C , calculation would give it 2.19 molecules per cell. Its composition is therefore considered to be in doubt. The space group is D_{3d}^5 .

(bv) A rhombohedral unit containing one molecule has been found for aluminum carbide, Al_4C_3 . It is said that the Al atoms are in two sets of special positions: (c) $\pm(uuu)$ of D_{3d}^5 with $u_1=0.293$ and $u_2=0.128$. Two of the three C atoms are in another set with $u'=0.217$; the third is at the origin (a) 000.

New Structures of the Type $R_x(MX_2)_y$

(ca) The pseudo-tetragonal unit assigned to $AgClO_2$ is supposed to include 16 molecules.

(cb) The cell described for the monoclinic sulfide **miargyrite**, $AgSbS_2$, contains eight molecules. The space group is reported to be C_{2h}^6 .

(cc) The possibly orthorhombic mineral **polybasite** $(Ag, Cu)_2Sb_2S_4$, has been given an eight-molecule cell. A space group assignment is V_h^{19} .

(cd) The orthorhombic unit of CaB_2O_4 contains four molecules. An atomic arrangement found from photographic data places atoms in the following positions of V_h^{14} :

Ca: (c) $\frac{1}{4}0u$; $\frac{3}{4}0\bar{u}$; $\frac{1}{4}, \frac{1}{2}, u+\frac{1}{2}$; $\frac{3}{4}, \frac{1}{2}, \frac{1}{2}-u$ with $u=0.26$

B: (d) xyz ; $x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$; $\bar{x}, y+\frac{1}{2}, \frac{1}{2}-z$; $\frac{1}{2}-x, \bar{y}, z$; $\bar{x}\bar{y}\bar{z}$; $\frac{1}{2}-x, y+\frac{1}{2}, z+\frac{1}{2}$;
 $x, \frac{1}{2}-y, z+\frac{1}{2}$; $x+\frac{1}{2}, y, \bar{z}$ with $x=0.12, y=0.20, z=0.88$

O_1 : (d) $x_1y_1z_1$; etc. with $x_1=0.125, y_1=0.21, z_1=0.19$

O' : (d) $x'y'z'$; etc. with $x'=0.11, y'=0.09, z'=0.75$.

The axes of this description are the same as those of 1930, 352; the origin is in a symmetry center at $\frac{1}{4}0\frac{1}{4}$. The linked B-O tetrahedra which make up the framework of this crystal can be seen from Figure 292a and b.

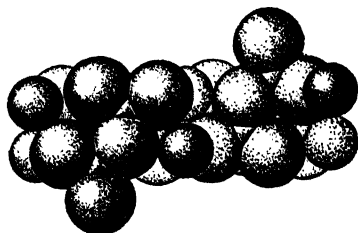
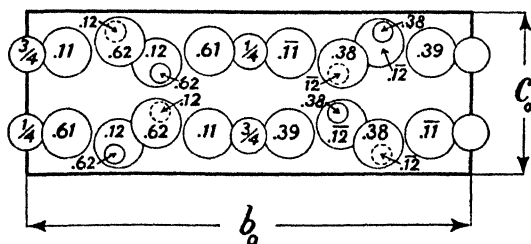


FIG. 292a.—(left) Atoms in the unit prism of CaB_2O_4 , projected on the a -face. The largest circles are O atoms; intermediate ones are Ca.

FIG. 292b.—(right) A packing drawing of a with Ca and O atoms having their ionic radii. The way the BO_4 tetrahedra are linked together by sharing oxygen atoms is clearly seen.

(ce) The pseudo-cube ascribed to $\text{Ca}(\text{ClO}_2)_2$ is bimolecular.

(cf) The orthorhombic unit of **emphlectite**, CuBiS_2 , contains four molecules; its space group is V_h^{16} . The corresponding antimony compound wolfsbergite, CuSbS_2 , is structurally isomorphous.

(cg) A redetermination of the structure of **chalcopyrite**, CuFeS_2 , has led to a somewhat more complicated arrangement. The unit prism, with the same base, has twice the previous height and contains four molecules. Atoms, in special positions of V_d^{12} , are at:

Cu: (a) $000; \frac{1}{2}0\frac{1}{4}; \frac{1}{2}\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{3}{4}$, Fe: (b) $00\frac{1}{2}; \frac{1}{2}0\frac{3}{4}; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{4}$
 S: (d) $\frac{1}{4}u\frac{5}{8}; u\frac{3}{4}\frac{7}{8}; \frac{3}{4}\bar{u}\frac{1}{8}; \bar{u}\frac{1}{4}\frac{7}{8}; \frac{3}{4}, u+\frac{1}{2}, \frac{5}{8}; u+\frac{1}{2}, \frac{1}{4}, \frac{3}{8}; \frac{1}{4}, \frac{1}{2}-u, \frac{5}{8}; \frac{1}{2}-u, \frac{3}{4}, \frac{3}{8}$

with $u=0.27$. The resulting atomic separations, $\text{Cu-S}=2.32 \text{ \AA}$, $\text{Fe-S}=2.20 \text{ \AA}$, are those to be expected from neutral atoms (Figure 293a and b).

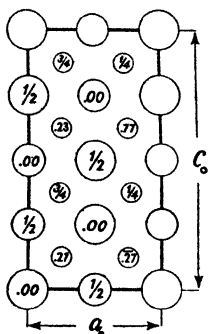


FIG. 293a.—(left) The new arrangement found for chalcopyrite, CuFeS_2 , as projected upon an a -face. Cu atoms are at the origin; intermediate circles are the Fe and the smallest circles the S atoms.

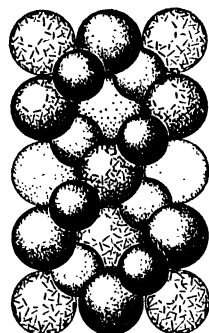


FIG. 293b.—(right) A packing drawing of CuFeS_2 giving the atoms their neutral radii. The line-shaded spheres are Cu.

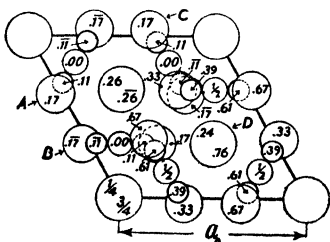


FIG. 294a.—(left) A basal projection of the atoms in the hexagonal unit of the structure found for $\text{KAg}(\text{CN})_2$. The largest circles are K atoms, the small heavy ones are C; of the intermediate circles the smaller represent the Ag atoms.

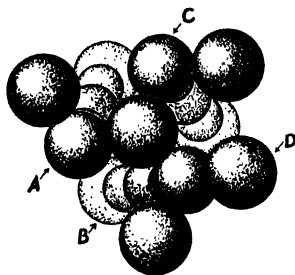


FIG. 294b.—(right) A packing drawing showing half the contents of the unit prism of $\text{KAg}(\text{CN})_2$. Corresponding atoms in a and b are designated by the same letters. Potassium and silver (line-shaded) atoms have their ionic radii but the sizes of C and N are probably without real significance.

(ch) The six-molecule unit found for $\text{KAg}(\text{CN})_2$ has an arrangement based on D_{3d}^2 . Its atomic positions have been given as (Figure 294):

K: (b) $00\frac{1}{4}; 00\frac{3}{4}$ K': (f) $\frac{1}{3}\frac{2}{3}u; \frac{1}{3}\frac{2}{3}\bar{u}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}-u; \frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}$ with $u=0.260$
 Ag: (h) $u\bar{u}0; 2\bar{u}, \bar{u}, 0; u, 2u, 0; \bar{u}u\frac{1}{2}; 2u, u, \frac{1}{2}; \bar{u}, 2\bar{u}, \frac{1}{2}$ with $u=0.167$
 C: (i) $xyz; y-x, \bar{x}, z; \bar{y}, x-y, z; x, x-y, \bar{z}; \bar{y}\bar{x}\bar{z}; y-x, y, \bar{z}; \bar{x}, \bar{y}, \frac{1}{2}-z;$
 $x-y, x, \frac{1}{2}-z; y, y-x, \frac{1}{2}-z; \bar{x}, y-x, z+\frac{1}{2}; y, x, z+\frac{1}{2}; x-y, \bar{y}, z+\frac{1}{2}$

with $x=0.295, y=\frac{1}{3}, z=0.109$

N: (i) $x'y'z'$; etc. with $x'=0.365, y'=\frac{1}{3}, z'=0.167$.

In all other cyanides it has not been possible to establish the separate positions of carbon and nitrogen. Instead the cyanide radical seems to have the spatial characteristics of a sphere with a radius substantially that of the bromide ion. For this reason it is not clear how much significance is to be attached to the C and N parameters stated above and to the short K-N separation (2.56 Å) that results.

(c) The unit cube assigned to $K_2Fe_2O_4$ is reported to contain four molecules.

(c) Eight molecules are associated with the hexagonal prism of $KFeS_2$.

(ck) Lithium ferrite, $Li_2Fe_2O_4$, is anisotropic if prepared below ca 600° C; above this temperature a cubic modification is produced which does not invert on cooling. The curious fact has been observed that its powder lines correspond to a unit containing one molecule. The intensities of these lines are explicable in terms of an NaCl arrangement [XI, (b)] of O atoms in (4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00$ and of Fe and Li atoms irregularly distributed among the positions (4b) $000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$.

(cl) Crystals of NH_4ClO_2 are said to have a tetragonal unit holding two molecules. The proposed atomic arrangement places atoms in the following special positions of C_{4v}^2 :

NH_4 : (a) $00u; \frac{1}{2}\frac{1}{2}u$ with $u=0$

Cl: (b) $0\frac{1}{2}u'; \frac{1}{2}0u'$ with $u'=\frac{1}{4}$

O: (c) $u_1, \frac{1}{2}-u_1, v; u_1+\frac{1}{2}, u_1, v; \bar{u}_1, u_1+\frac{1}{2}, v; \frac{1}{2}-u_1, \bar{u}_1, v$ with $v=\frac{1}{2}$.

A more detailed study of this structure would be instructive.

(cm) The original investigation of NH_4HF_2 (1932, 196) gave it the symmetry of V_h^{18} but failed to find an atomic arrangement. Recently the same data have been shown to be consistent with the following structure developed from V_h^7 :

N: (g) $\frac{1}{4}\frac{1}{4}u; \frac{1}{4}\frac{1}{4}\bar{u}; \frac{3}{4}\frac{3}{4}\bar{u}; \frac{3}{4}\frac{1}{4}u$ with $u=0.560$

F: (e) $u'00; \bar{u}'00; \frac{1}{2}-u', \frac{1}{2}, 0; u'+\frac{1}{2}, \frac{1}{2}, 0$ with $u'=0.142$

F: (h) $\frac{1}{2}u_1v; \frac{1}{2}\bar{u}_1\bar{v}; 0, \frac{1}{2}-u_1, v; 0, u_1+\frac{1}{2}, \bar{v}$ with $u_1=0.132, v=0.135$.

These axes, abc , and $X'Y'Z'$ of 1930, 352 are connected by the relations $a=X', b=Z', c=Y'$. The pairs of fluorine atoms belonging to an HF_2 ion are, as should be expected, especially close together with $F-F=2.37$ Å

(Figure 295a and b). It is customary to assume that the hydrogen atom in these acid fluorides lies midway between the two fluorine atoms on a line joining their centers; such an assumption cannot of course be proved by means of X-rays.

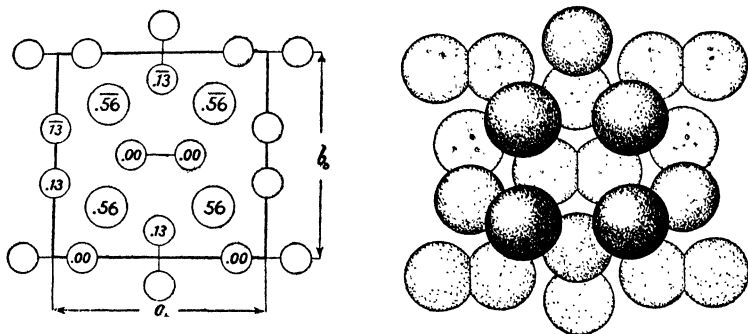


FIG. 295a.—(left) The structure found for NH_4HF_2 projected upon the c -face of its orthorhombic unit. The larger circles are the NH_4 groups.

FIG. 295b.—(right) A packing drawing of the NH_4 and HF_2 ions in NH_4HF_2 .

(cn) **Sodium ferrite** is rhombohedral with the CsCl_2I structure (d). Atoms of the single NaFeO_2 molecule in the unit rhombohedron have the coordinates: Na at 000; Fe at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; O at uuu ; $\bar{u}\bar{u}\bar{u}$ with $u=0.22$.

(co) From photographic data it has been concluded that the atoms in the two-molecule orthorhombic unit of NaNO_2 are in the following special positions of C_{2v}^{20} :

Na: (a) $0u0$; $\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}$ with $u=0.583$

N: (a) $0u'0$; $\frac{1}{2}$, $u'+\frac{1}{2}$, $\frac{1}{2}$ with $u'=0.083$

O: (d) $0u_1v$; $0u_1\bar{v}$; $\frac{1}{2}$, $u_1+\frac{1}{2}$, $v+\frac{1}{2}$; $\frac{1}{2}$, $u_1+\frac{1}{2}$, $\frac{1}{2}-v$ with $u_1=0$ and $v=0.194$.

The coordinates of this description can be derived from those of 1930, 352, p. 56 by an interchange of Y' and Z' . The simple structure outlined above is illustrated in Figure 296a and b. The N-O separation in its non-linear NO_2 ion is 1.13 Å; the Na-O distance, ca 2.48 Å, is substantially that found in NaNO_3 .

(cp) The supposed pseudo-tetragonal unit of $\text{Pb}(\text{ClO}_2)_2$ is reported to contain one molecule.

(cq) A monoclinic cell for TlAsS_2 with the dimensions of the table would enclose eight molecules. The space group has been given as either C_{2h}^4 or C_{2h}^5 .

(cr) Photographic observations have been used to assign an atomic arrangement to crystals of ammonium hypophosphite, $\text{NH}_4\text{H}_2\text{PO}_2$. Ac-

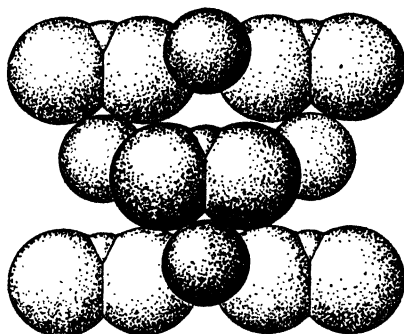
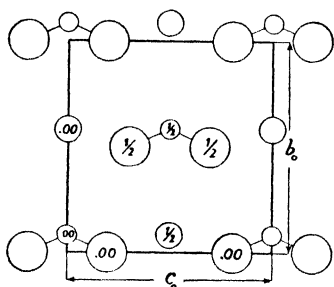


FIG. 296a.—(left) The orthorhombic grouping found for NaNO_2 projected on its a -face. Atoms of the non-linear NO_2 groups are joined by light lines; intermediate circles designate the Na atoms.

FIG. 296b.—(right) A packing drawing of a .

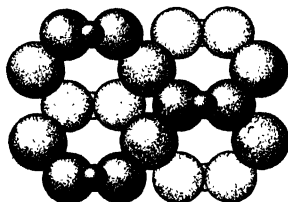
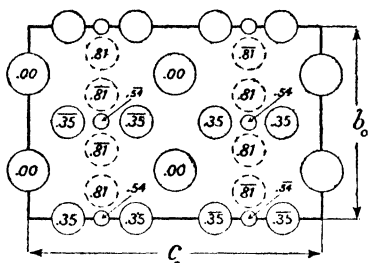


FIG. 297a.—(left) The structure chosen for $\text{NH}_4\text{H}_2\text{PO}_2$ projected on the a -face of its orthorhombic cell. K, O and P atoms are shown as large, intermediate and small circles. Proposed positions for the hydrogen atoms are indicated by the dashed circles.

FIG. 297b.—(right) A packing drawing of a showing the positions of the NH_4 and PO_2 groups.

cording to this structure (Figure 297) which places four molecules in the orthorhombic unit, atoms are in the following special positions of V_h^{21} :

$$\begin{aligned} \text{NH}_4: & \text{(a)} \pm(0\frac{1}{4}0); \pm(0\frac{3}{4}\frac{1}{2}) & \text{P: (g)} & \pm(u0\frac{1}{4}); \pm(u\frac{1}{2}\frac{3}{4}) \\ \text{O: (m)} & \pm(u'0v'); \pm(u'\frac{1}{2}v'); \pm(u', 0, \frac{1}{2}-v'); \pm(u', \frac{1}{2}, v'+\frac{1}{2}). \end{aligned}$$

The axes of this description (abc) arise from those of 1930, 352, p. 67 ($X'Y'Z'$) by transferring the origin to a center of symmetry and using the transformation $a=Z'$, $b=X'$, $c=Y'$.

The chosen parameters $u(\text{P})=0.541$, $u'(\text{O})=0.347$, $v'=0.136$ give an $\text{NH}_4\text{-O}$ separation (2.81 Å) which is unusually short. This has been considered to show that the NH_4 groups are not rotating; such an interpretation could be convincing only if the correctness of the selected parameters were supported by more quantitative evidence than is now available.

Suggested hydrogen positions, which would bind each atom to two NH_4 groups and one phosphorus atom are (m) u_10v_1 ; etc. with $u_1=0.805$, $v_1=0.142$; they cannot of course be checked by X-ray observations.

Chapter XVA. Structures of the Type $R_x(MX_3)_y$

(*ab*) The parameters of Table I have been assigned to the atoms in divalent nitrates having the structure (*s*) characteristic of $Ba(NO_3)_2$. It has been suggested (1931, 265) that at ordinary temperatures the nitrate groups in $Ca(NO_3)_2$ are rotating but data in support of this idea have not been published.

TABLE I. PARAMETERS FOR CRYSTALS OF THE ALKALINE EARTH NITRATES

<i>Crystal</i>	<i>u(N)</i>	<i>x(O)</i>	<i>y(O)</i>	<i>z(O)</i>
$Ba(NO_3)_2$	0.150	0.220	0.204	0.026
$Ca(NO_3)_2$.161	.247	.207	.033
$Pb(NO_3)_2$.156	.234	.209	.033
$Sr(NO_3)_2$.159	.236	.209	.032

(*ac*) The unit prism of **bromlite** (alstonite), $BaCa(CO_3)_2$, contains two molecules. It is similar in shape to the orthorhombic cells of barite and aragonite with dimensions lying between them. Nevertheless this mineral is thought to be a compound rather than a solid solution.

(*ad*) The monoclinic **barytocalcite**, also $BaCa(CO_3)_2$, has been assigned a two-molecule unit. The space group is reported as C_2^2 .

(*ae*) The three hexagonal carbonates **synchisite**, $CaCO_3 \cdot RFCO_3$, **parisite**, $CaCO_3 \cdot 2RFCO_3$, and **cordylite**, $BaCO_3 \cdot 2RFCO_3$ (R is a mixture of trivalent rare earth atoms, Ce, La, etc.) have unit prisms with bases of about equal size but with very different heights. Closely related atomic arrangements, which however need further confirmation, have been proposed for these minerals. The following atomic coordinates are necessary for their description:

$$\begin{array}{ll}
 \text{(a) } 00w; 0, 0, w+\frac{1}{2} & \text{(b) } 00v; 00\bar{v}; 0, 0, v+\frac{1}{2}; 0, 0, \frac{1}{2}-v \\
 \text{(c) } \frac{1}{3}\frac{2}{3}u; \frac{2}{3}\frac{1}{3}\bar{u}; \frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-u & \text{(d) } \frac{2}{3}\frac{1}{3}t; \frac{1}{3}, \frac{2}{3}, t+\frac{1}{2}.
 \end{array}$$

Oxygen atoms have not been located; the other atomic positions together with the corresponding parameters (in parentheses) are listed in Table II.

TABLE II. ATOMIC POSITIONS AND PARAMETERS GIVEN TO THE ATOMS IN SYNCHISITE, PARISITE AND CORDYLITE

Substance	2 Ca (or Ba)	2 F	2 R	2 CO ₃	4 R	4 F	4 CO ₃
Synchisite	a	d	a	—	—	—	c
CaCO ₃ ·RFCO ₃	(w=0)	($\frac{1}{2}$)	($\frac{1}{2}$)	—	—	—	(-0.117)
Parisite	a	—	—	d	b	c	c
CaCO ₃ ·2RFCO ₃	(0)	—	—	($\frac{1}{2}$)	(0.163)	(0.163)	(-0.076)
Cordylite	a	—	—	d	c	b	c
BaCO ₃ ·2RFCO ₃	(0)	—	—	($\frac{1}{2}$)	($\frac{1}{2}$)	($\frac{1}{2}$)	(-0.07)

(af) A new structure has been proposed for **bastrnäsite**, (**Ce, La, . . .**) **FCO₃**, based on D_{3h}^4 instead of D_{3h}^3 . Its atoms have been put in the positions:

- 6 R: (g) uu0; etc. of 1930, 352, p. 159, with $u = \frac{2}{3}$
 2 F: (a) 000; $00\frac{1}{2}$ 4 F: (f) $\frac{1}{3}\frac{2}{3}u$; etc. with $u = ca\ 0$.
 12 O: (i) xyz; etc. with $x=y=ca\ \frac{1}{3}$, $z=ca\ \frac{1}{2}$
 6 O: (h) $uv\frac{1}{2}$; etc. with u and v undetermined
 6 C: (h) $u'v'\frac{1}{2}$; etc. with u' and v' undetermined.

(ag) Parameters have been determined for the atoms in **KNO₃** and **PbCO₃**. As Table III indicates they are almost identical with one another and with those previously found for aragonite (b) (see p. 272 of book).

TABLE III. PARAMETERS OF THE ATOMS IN KNO₃, PbCO₃, AND ARAGONITE

Atom	KNO ₃			PbCO ₃			CaCO ₃		
	x	y	z	x	y	z	x	y	z
K, Pb, Ca	0	0.416	0	0	0.417	0	0	0.417	0
N, C, C	0	.75	$\frac{1}{2}$	0	.764	0.153	0	.75	$\frac{1}{2}$
O(1)	0	.883	$\frac{1}{2}$	0	.908	.153	0	.917	$\frac{1}{2}$
O(2)	0.194	.686	$\frac{1}{2}$	0.205	.692	.153	0.23	.67	$\frac{1}{2}$

(ah) A structure based on photographic data has been deduced for the iodine and oxygen atoms in **LiIO₃**. These atoms in the two-molecule unit are placed in the following special positions of D_6^6 :

- I: (c) $\frac{1}{3}\frac{2}{3}\frac{1}{2}$; $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ O: (g) uu0; $0\bar{u}0$; $\bar{u}00$; $\bar{u}\bar{u}\frac{1}{2}$; $0u\frac{1}{2}$; $u0\frac{1}{2}$ with $u = \frac{1}{3}$.

If the lithium atoms are in (b) $00\frac{1}{4}$; $00\frac{3}{4}$ a reasonable Li-O separation, 2.23 Å, is obtained. It should be noticed (Figure 298) that this arrange-

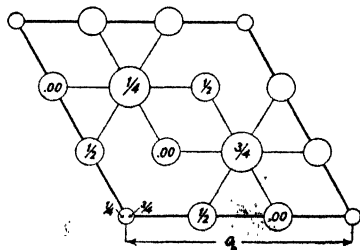


FIG. 298.—A basal projection of the arrangement proposed for **LiIO₃**. The Li atoms are represented by the smallest, the I by the largest circles. The absence of **IO₃** ions in this grouping is evident.

TABLE IV. THE CRYSTAL STRUCTURES OF THE COMPOUNDS $R_x(MX_3)_y$

Substance, symmetry and structure type		a_o	c_o or α	References
AgFO ₂	Tetragonal (?)	5.33	6.08	1933, 117.
BaCO ₃	Ortho- rhombic	KNO ₃ (<i>b</i>) 5.2556	6.5490 $b_o=8.8345$	1931, 89.
BaCa(CO ₃) ₂ (Bromlite)	Ortho- rhombic	(<i>ac</i>) 8.77	6.11 $b_o=4.99$	1930, 111b.
BaCa(CO ₃) ₂ (Barytocalcite)	Monoclinic	(<i>ad</i>) 8.15	6.58 $b_o=5.22, \beta=83^\circ 52'$	1930, 111c.
BaCO ₃ ·2RfCO ₃ (Cordylite)	Hexagonal	(<i>ae</i>) 4.35	22.8	1931, 337.
BaCeO ₃	Cubic	CaTiO ₃ (<i>d</i>) 4.377		1934, 112.
Ba(NO ₃) ₂	Cubic	Ba(NO ₃) ₂ (<i>s</i>), (<i>ab</i>)		1931, 460.
BaThO ₃	Cubic	CaTiO ₃ (<i>d</i>) 4.480		1934, 112.
BaZrO ₃	Cubic	CaTiO ₃ (<i>d</i>) 4.176		1934, 112.
CaCO ₃ (Calcite)	Hexagonal	(<i>ap</i>)		1931, 34, 35, 122; 1934, 283.
CaCO ₃ ·RfCO ₃ (Synchisite)	Hexagonal	(<i>ae</i>) 4.094	18.20	1931, 337.
CaCO ₃ ·2RfCO ₃ (Parisite)	Hexagonal	(<i>ae</i>) 4.094	27.93	1931, 337.
CaMg(CO ₃) ₂ (Dolomite)	Hexagonal	(<i>v</i>) 6.050± 0.004	46°54'	1930, 398.
Ca(NO ₃) ₂	Cubic	Ba(NO ₃) ₂ (<i>s</i>), (<i>ab</i>)		1931, 265, 460.
CaSn(BO ₃) ₂ (Nordenskiöldite)	Hexagonal	(<i>v</i>) 6.24	45°44'	1934, 219.
CdTiO ₃ (low temp. form)	Hexagonal	FeTiO ₃ (<i>ax</i>) 5.82	53°36'	1934, 216.
(Ce, La . . .). FCO ₃ (Bastnäsite)	Hexagonal	(<i>af</i>) 7.094	9.718	1931, 336.
CoCO ₃	Hexagonal	NaN ₃ (<i>a</i>)		1932, 14.
CoTiO ₃	Hexagonal	FeTiO ₃ (<i>ax</i>) 5.49	54°42'	1934, 216.
CsNO ₃	Hexagonal	(<i>aw</i>) 10.74	7.68	1934, 273.
Cs ₂ S ₂ O ₈	Hexagonal	(<i>au</i>) 6.326	11.535	1932, 187.
FeCO ₃ * (Siderite)	Hexagonal	NaN ₃ (<i>a</i>) 5.754	47°25'	1932, 167.
FeTiO ₃ (Ilmenite)	Hexagonal	FeTiO ₃ (<i>ax</i>) 5.52	54°50'	1934, 14, 216.
H ₃ BO ₃	Triclinic	(<i>ay</i>) 7.04	6.56† $b_o=7.04$	1934, 304.
InBO ₃	Hexagonal	NaN ₃ (<i>a</i>) 5.841	48°10'	1932, 167.
KCbO ₃	Cubic (?)	CaTiO ₃ (<i>d</i>) 4.005		1932, 371.
KNO ₃	Ortho- rhombic	KNO ₃ (<i>b</i>), (<i>ag</i>) 5.43	6.45 $b_o=9.17$	1931, 102.

* 92.5% FeCO₃, 6.1% MnCO₃.† For H₃BO₃, $\alpha=92^\circ 30'$, $\beta=101^\circ 10'$, $\gamma=120^\circ$.

Substance, symmetry and structure type			a_o	c_o or α	References
$K_2S_2O_6$	Hexagonal	(<i>av</i>)	9.756	6.274	1931, 30, 220; 1932, 186, 201; 1933, 210, 211.
KTaO ₃	Cubic (?)	CaTiO ₃ (<i>d</i>)	3.981		1932, 371.
LaBO ₃	Ortho- rhombic	KNO ₃ (<i>b</i>)	5.10	5.83 $b_o=8.22$	1932, 167.
LiIO ₃	Hexagonal	(<i>ah</i>)	5.469	5.155	1931, 499.
MgTiO ₃	Hexagonal	FeTiO ₃ (<i>ax</i>)	5.54	54°39'	1934, 216.
Mn ₃ As ₂ O ₆ (Armandgite)	Hexagonal	(<i>ai</i>)	13.44	8.72	1933, 5.
MnTiO ₃	Hexagonal	FeTiO ₃ (<i>ax</i>)	5.62	54°16'	1934, 216.
NH ₄ IO ₃	Cubic	CaTiO ₃ (<i>d</i>)	4.5		1932, 158.
NH ₄ NO ₃ (I) (169.5° to 125.2° C range)	Cubic	(<i>aj</i>)	4.40		1931, 265; 1932, 204.
NH ₄ NO ₃ (II) (125.2° to 84.2° C range)	Tetragonal	(<i>ak</i>)	5.75	5.00	1931, 265; 1932, 204.
NH ₄ NO ₃ (III) (84.2° to 32.3° C range)	Ortho- rhombic	(<i>al</i>)	7.06	5.80 $b_o=7.66$	1932, 204.
NH ₄ NO ₃ (IV) (32.3° to -18° C range)	Ortho- rhombic	(<i>am</i>)	5.75	4.96 $b_o=5.45$	1932, 204, 470.
NH ₄ NO ₃ (V) (below -18° C)	Hexagonal	(<i>an</i>)	5.75	15.9	1932, 204.
NaCbO ₃	Cubic (?)	CaTiO ₃ (<i>d</i>)	3.889		1932, 371.
NaHCO ₃	Monoclinic	(<i>ao</i>)	7.51	3.53 $b_o=9.70, \beta=93^\circ 19'$	1933, 518.
NaNO ₃	Hexagonal	NaNO ₃ (<i>a</i>), (<i>ap</i>)			1931, 266; 1932, 49; 1933, 492; 1934, 235.
N ₂ SO ₃	Hexagonal	(<i>aq</i>)	5.441	6.133	1931, 500.
NaSbO ₃ ·4BeO (Swedenborgite)	Hexagonal	(<i>y</i>), (<i>as</i>)			1933, 3.
NaTaO ₃	Cubic (?)	CaTiO ₃ (<i>d</i>)	3.881		1932, 371.
NaWO ₃ (Cubic Na-W Bronze)	Cubic	CaTiO ₃ (<i>d</i>), (<i>ar</i>)	3.83		1932, 250.
Na ₂ (WO ₃) ₅ (?) (Blue Na-W Bronze)	Tetragonal	(<i>ar</i>)	17.5	3.80	1932, 251.
(Na, Ce, Ca). (Ti, Cb)O ₃ (Loparite)	Cubic (?)	CaTiO ₃ (<i>d</i>)	3.854		1930, 391.
NiTiO ₃	Hexagonal	FeTiO ₃ (<i>ax</i>)	5.45	55°8'	1934, 216.
PbCO ₃ (Cerussite)	Ortho- rhombic	KNO ₃ (<i>b</i>), (<i>aq</i>)	5.166	6.146 $b_o=8.468$	1933, 101.
Pb(NO ₃) ₂	Cubic	Ba(NO ₃) ₂ (<i>s</i>), (<i>ab</i>)			1931, 460.
RbNO ₃	Ortho- rhombic	(<i>at</i>)	18.08	7.38 $b_o=10.45$	1933, 351.
Rb ₂ S ₂ O ₆	Hexagonal	K ₂ S ₂ O ₆ (<i>av</i>)	10.144	6.409	1931, 220; 1932, 186.
ScBO ₃	Hexagonal	NaNO ₃ (<i>a</i>)	5.782	48°28'	1932, 167.

Substance, symmetry and structure type			a_o	c_o or α	References
SrHfO ₃	Cubic	CaTiO ₃ (<i>d</i>)	4.069		1933, 204.
Sr(NO ₃) ₂	Cubic	Ba(NO ₃) ₂ (<i>s</i>), (<i>ab</i>)			1931, 460.
SrZrO ₃	Cubic	CaTiO ₃ (<i>d</i>)	4.089		1933, 204.
YBO ₃	Hexagonal	NaNO ₃ (<i>a</i>)	6.44	46°17'	1932, 167.
ZnCO ₃	Hexagonal	NaNO ₃ (<i>a</i>)	5.669	48°26'	1932, 167.

ment does not provide either simple or complex iodate ions such as would be expected on chemical grounds; instead each iodine atom is made equidistant from six oxygen atoms (I-O=2.23 Å=Li-O). For this reason a further study of LiIO₃ must sometime be made.

(*ai*) The hexagonal unit of **armangite**, **Mn₃As₂O₆**, recorded in Table IV would contain nine molecules. It is thought that the true unit is probably rhombohedral, with a space group that is C_{3v}^5 , D_3^7 or D_{3d}^5 .

(*aj*) The **highest** temperature modification of **NH₄NO₃** seems to give the simple diffraction pattern required by a one-molecule cube in which N atoms and NO₃ groups have a body-centered CsCl grouping [XI, (*a*)]. Individual crystals of this modification grow so fast that good intensity data could not be obtained but the single molecule unit has been taken as evidence for a rotating NO₃ group.

(*ak*) The unit of the **second**, tetragonal, form of **NH₄NO₃** contains two molecules. Even at 100° C these crystals grew too fast to yield good diffraction data and no *z* parameters could be established. The *x* and *y* parameters are said to be the following:

$$\begin{array}{lll} \text{NH}_4: & 00?; \frac{1}{2}\frac{1}{2}? & \text{N: } 0\frac{1}{2}?; \frac{1}{2}0? & \text{O: } 0\frac{1}{2}?; \frac{1}{2}0? \\ & \text{O: } xy?; \bar{x}\bar{y}?; \bar{y}\bar{x}?; y\bar{x}? & \text{with } x=0.14, y=0.36. \end{array}$$

(*al*) The **third** modification of **NH₄NO₃** has a four-molecule orthorhombic prism and a structure based on V_h^{16} . Choosing the same axial orientation that was used for cementite [XIV, (*o*)] atoms have been found to be in the positions:

$$\begin{array}{ll} \text{NH}_4: & \text{(c) } uv\frac{1}{4}; \text{ etc. (book, p. 266) with } u=0.30, v=0.52 \\ \text{N:} & \text{(c) } u'v'\frac{1}{4}; \text{ etc. with } u'=-0.09, v'=-0.19 \\ \text{O:} & \text{(c) } u_1v_1\frac{1}{4}; \text{ etc. with } u_1=-0.19, v_1=-0.05 \\ \text{O:} & \text{(d) } xyz; \text{ etc. with } x=-0.07, y=-0.27, z=0.06. \end{array}$$

This arrangement is illustrated in Figure 299a and b.

(*am*) Two separate determinations have shown that the two molecules in the orthorhombic unit of **NH₄NO₃** which is stable at ordinary temperatures are arranged according to the unusual space group V_h^{18} . With axes chosen as in Table IV they agree in placing atoms in the following special positions:

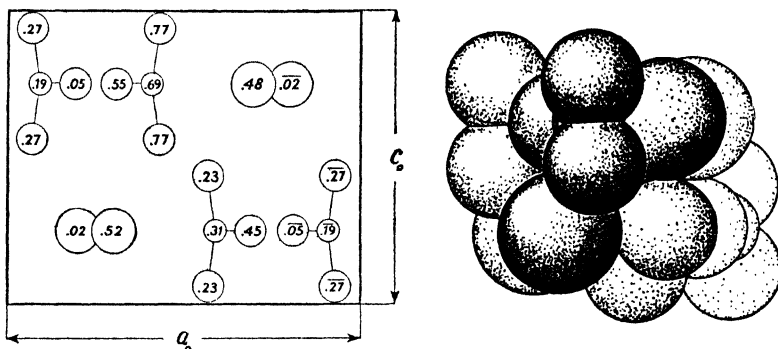
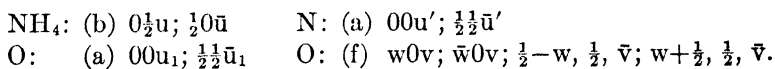


FIG. 299a.—(left) The atoms of the third modification of NH_4NO_3 projected on the b-face of its orthorhombic unit. Atoms of the NO_3 groups are joined by light lines.

FIG. 299b.—(right) A packing drawing of a .



The origin used in 1932, 470 is displaced one half along the c-axis; therefore though the parameters as listed in Table V are different, the atomic arrangements found in these two investigations are nearly identical. This can be seen from Figure 300a, wherein the unit of 1932, 204 is outlined by heavy lines, that of 1932, 470 using dotted lines.

TABLE V. PARAMETERS OF THE ATOMS IN NH_4NO_3
(Room Temperature Form IV)

Determination	$u(\text{NH}_4)$	$u'(\text{N})$	$u_1(\text{O})$	w	v
1932, 204	0.57	0.03	0.28	0.19	-0.095
1932, 470	.097	.500	.75	.183	.375

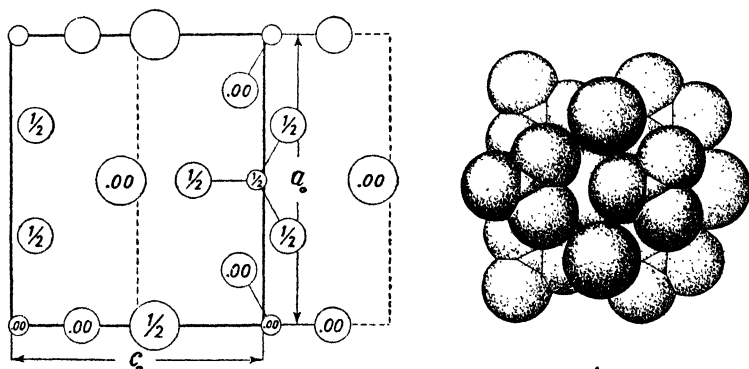


FIG. 300a.—(left) The structure of the fourth, room temperature, form of NH_4NO_3 projected on its b-face. The unit cells of the two determinations are indicated by full and by dotted lines. The largest circles are NH_4 ions, the smallest are N atoms.

FIG. 300b.—(right) A packing drawing of a .

(an) The **fifth** modification of NH_4NO_3 (stable below -18°C) has been given a hexagonal, or pseudo-hexagonal, unit containing six molecules. No X-ray evidence was found which indicated the gradual transition at -60°C .

(ao) The monoclinic unit chosen for NaHCO_3 contains four molecules. Using photographic spectral data it has been given an atomic arrangement with all atoms in general positions of C_{2h}^5 (Figure 301): (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$. The selected parameters are listed in Table VI. In this structure the distance between oxygen atoms in adjacent CO_3 groups is 2.55 Å. Such a close approach has been thought to mean that these atoms are bound by an intermediate hydrogen atom which then would be at $x=0.319, y=0.250, z=0.064$. The atomic parameters of Table VI and with them this evidence for the existence of a hydrogen bond should be confirmed by more quantitative intensity data.

The coordinates used in this description refer to axes so chosen that the gliding component is along the diagonal to two of them. In the conventional description it is along one axis.

TABLE VI. PARAMETERS OF THE ATOMS IN NaHCO_3

Atom	x	y	z
Na	0.278	0.0	0.708
C	.069	.236	.314
O(1)	.069	.367	.314
O(2)	.200	.169	.183
O(3)	.939	.169	.444

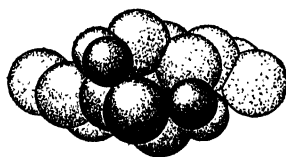
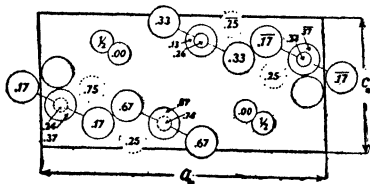


FIG. 301a.—(left) Atoms in the proposed structure for NaHCO_3 projected on the b -face of its monoclinic unit. The large O and small C atoms of the CO_3 groups are joined by light lines; positions thought probable for the hydrogen atoms are indicated by the dotted circles.

FIG. 301b.—(right) A packing drawing showing the small Na^+ and the larger CO_3 groups of a .

(ap) X-ray photographs of NaNO_3 made at various temperatures up to 280°C have been interpreted as showing that the NO_3 group is rotating at high temperature. At 280°C the unit rhombohedron has the dimensions $a_0 = 6.56 \text{ \AA}$, $\alpha = 45^\circ 35'$.

Similar measurements of unit cell size at higher temperatures, as well as Laue photographs up to 600°C , have been made of calcite (CaCO_3).

(aq) Using data derived from twinned crystals the atoms in the two-molecule unit of Na_2SO_3 have been placed in the following positions of C_{3i}^1 (Figure 302):

$$\begin{array}{lll} \text{Na:} & \text{(a) } 000 & \text{(b) } 00\frac{1}{2} & \text{(d) } \frac{1}{3}\frac{2}{3}u; \frac{2}{3}\frac{1}{3}\bar{u} \text{ with } u=0.67 \\ \text{S:} & \text{(d) } \frac{1}{3}\frac{2}{3}u'; \frac{2}{3}\frac{1}{3}\bar{u}' & \text{with } u'=0.17 \\ \text{O:} & \text{(g) } xyz; y-x, \bar{x}, z; \bar{y}, x-y, z; \bar{x}\bar{y}\bar{z}; x-y, x, \bar{z}; y, y-x, \bar{z} \end{array}$$

with $x=0.14$, $y=0.40$, $z=0.25$.

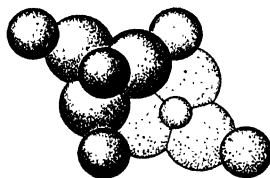
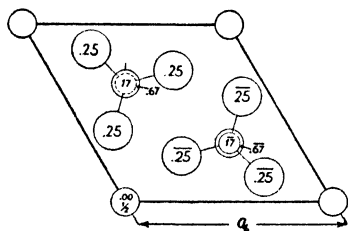


FIG. 302a.—(left) A basal projection of atoms in the hexagonal unit of Na_2SO_3 . The smallest circles are the S and the largest the O atoms.

FIG. 302b.—(right) A packing drawing of a . One S atom (at $z=0.17$) is shown lying above the plane of its three O atoms.

(ar) The analyses of cubic **Na-W bronzes** run from $\text{Na}_2\text{W}_2\text{O}_6$ to apparently $\text{Na}_2\text{W}_7\text{O}_{21}$. This variation in composition is thought due to the gradual replacement of sodium by hydrogen.

Blue Na-W bronzes are made by the weak reduction of NaWO_3 by zinc or hydrogen. The composition approaches that stated in Table IV.

(as) The formula previously given to the mineral **swedenborgite** is wrong due to the interpretation of its beryllium as aluminum. Its unit contains two of the new molecules $\text{NaSbO}_3 \cdot 4\text{BeO}$. One or the other of the following two structures developed from C_{6v}^4 has been considered to be correct:

$$\begin{array}{ll} \text{Na:} & \text{(a) } 00u_1; 0, 0, u_1+\frac{1}{2} \text{ with } u_1=0 & \text{or} \\ & \text{(b) } \frac{1}{3}\frac{2}{3}u'; \frac{2}{3}, \frac{1}{3}, u'+\frac{1}{2} \text{ with } u'=\frac{2}{4} \\ \text{O:} & \text{(b) or (a)} \\ \text{O:} & \text{(c) } u\bar{u}v; 2\bar{u}, \bar{u}, v; u, 2u, v; \bar{u}, u, v+\frac{1}{2}; 2u, u, v+\frac{1}{2}; \\ & \bar{u}, 2\bar{u}, v+\frac{1}{2} \text{ with } u=\frac{1}{2}, v=0 \\ \text{O:} & \text{(c) } u''\bar{u}''v''; \text{ etc. with } u''=\frac{1}{6} \text{ and } v''=\frac{1}{4} \\ \text{Sb:} & \text{(b) } \frac{1}{3}\frac{2}{3}u_2; \frac{2}{3}, \frac{1}{3}, u_2+\frac{1}{2} \text{ with } u_2=\frac{1}{6}. \end{array}$$

(at) A reexamination of **RbNO₃** has led to a different structure. The large orthorhombic unit of Table IV contains 18 molecules. The crystal, however, is pseudo-hexagonal; if its slight departure from this higher symmetry is neglected, the data are those to be expected from a structure with

$a_o = 10.45$, $c_o = 7.38$, having nine molecules in the unit and C_{3v}^2 as space group. The previously chosen unit was rhombohedral (or pseudo-rhomboidal) with an arrangement developed from C_{3v}^5 [see (n), p. 279 of book].

(*av*) The unit prism of $Cs_2S_2O_6$ contains two molecules; the space group is given as either D_6^6 or D_{3h}^4 . Cesium and sulfur atoms are assigned to the special positions:

$$\begin{array}{ll} Cs: (a) 000; 00\frac{1}{2} & Cs: (c) \frac{1}{3}\frac{2}{3}\frac{1}{4}; \frac{2}{3}\frac{1}{3}\frac{3}{4} \\ S: (f) \frac{1}{3}\frac{2}{3}u; \frac{2}{3}\frac{1}{3}\bar{u}; \frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-u \text{ with } u=0.70. \end{array}$$

No X-ray selection could be made between the two sets of oxygen positions that were considered possible.

(*av*) Four studies have been made of the structure of **potassium dithionate**, $K_2S_2O_6$. From them it is clear that the hexagonal unit contains three molecules and that atoms are in the following special positions of D_3^2 :

$$\begin{array}{ll} 2 S: (c) 00u; 00\bar{u} & 4 S \text{ in 2 sets of: } (d) \frac{1}{3}\frac{2}{3}u; \frac{2}{3}\frac{1}{3}\bar{u} \\ 3 K: (e) uu0; 0\bar{u}0; \bar{u}00 & 3 K: (f) uu\frac{1}{2}; 0\bar{u}\frac{1}{2}; \bar{u}0\frac{1}{2} \\ 18 O \text{ in 3 sets of: } (g) xyz; y-x, \bar{x}, z; \bar{y}, x-y, z; & \\ & yx\bar{z}; \bar{x}, y-x, \bar{z}; x-y, \bar{y}, \bar{z}. \end{array}$$

This crystal provides an instructive example of two very different arrangements (see oxygen parameters) that agree with the qualitative data from a group of spectral photographs. It has been shown that these data are about equally well explained by the two sets of parameters of Table VII. The second set (according to 1932, 201) gives so short a K-O separation, ca 2.2 Å, that it cannot be right. The satisfactory K-O distances, of ca 2.80 Å, yielded by the parameters of 1933, 210 suggest that they may be near the true values (Figure 303a and b).

(*aw*) The hexagonal unit which has been ascribed to $CsNO_3$ contains nine molecules. No atomic arrangement has been deduced but the curious observation has been made that its powder pattern is nearly identical with that of the cubic (or pseudo-cubic) KIO_3 and very similar to that of the cubic CsI . No change in pattern occurs on heating $CsNO_3$ up to 200° C.

TABLE VII. PARAMETERS FOR THE ATOMS OF $K_2S_2O_6$

Atom	Parameters according to					
	1933, 210			1932, 201 (<i>x and y interchanged</i>)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0	0	0.16	0	0	0.16
S(2)	$\frac{1}{3}$	$\frac{2}{3}$.59	$\frac{1}{3}$	$\frac{2}{3}$.59
S(3)	$\frac{1}{3}$	$\frac{2}{3}$.27	$\frac{1}{3}$	$\frac{2}{3}$.27
K(1)	0.375	0.375	0	0.39	0.39	0
K(2)	.69	.69	$\frac{1}{2}$.69	.69	$\frac{1}{2}$
O(1)	.165	.11	.23	.09	.18	.22
O(2)	.615	.17	.34	.48	.24	.35
O(3)	.505	.21	.80	.58	.42	.79

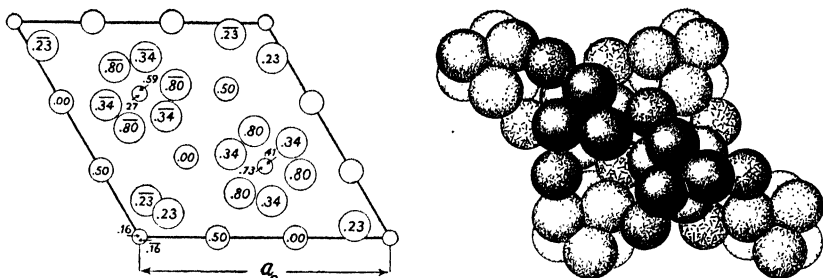
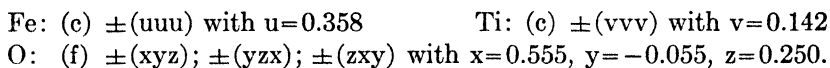


FIG. 303a.—(left) A basal projection of the atoms in the hexagonal unit of $K_2S_2O_6$. The largest circles are O, the smallest are S atoms.

FIG. 303b.—(right) A packing drawing of a . The K ions are indicated by line-shading.

(αx) The mineral **ilmenite**, $FeTiO_3$, has a rhombohedral structure similar to the Fe_2O_3 arrangement [XIII, (a)]. Its corresponding space group, C_{3i}^2 , is of lower symmetry because of the non-identity of its metal atoms but the two-molecule rhombohedra are of nearly the same size and shape. In $FeTiO_3$, atoms have been given the positions:



As might be expected from the close similarity in their cell sizes, it has been found that ilmenite and Fe_2O_3 form a continuous series of solid solutions (1934, 216).

Nickel titanate, $NiTiO_3$, has the ilmenite structure. The parameters assigned to its atoms are identical, within the limit of experimental error, with those of $FeTiO_3$.

Cadmium titanate, $CdTiO_3$, occurs in two forms. The previously described structure, isomorphous with $CaTiO_3$ (d), is found in material prepared by quenching from above $1000^\circ C$. Crystals made below this temperature are like $FeTiO_3$. The parameters given their atoms, $u(Cd)=0.342$, $v(Ti)=0.156$, $x=0.54$, $y=-0.03$, $z=0.26$, yield the short Cd-O distance of 2.24 Å but it is said that other values would make it shorter still.

(αy) The triclinic cell chosen for crystals of **boric acid**, H_3BO_3 , includes four molecules. If the space group is C_1^1 , as is undoubtedly the case, all atoms are in general positions $\pm(xyz)$. Boron and oxygen atoms have been assigned parameters (Table VIII) which yield a thoroughly platy structure. The resulting interatomic distances are B-O=1.36 Å and, between adjacent groups, O-O=2.71 Å. It is stated that this O-O separation is sufficiently below the normal 2.80 Å to show that hydrogen atoms are situated between them. Inasmuch as the entire determination of structure, involving many variable parameters, has been based on

THE STRUCTURE OF CRYSTALS

TABLE VIII. PARAMETERS FOR THE ATOMS OF H_3BO_3

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>
B(1)	0.653	0.430	0.25
B(2)	.319	.764	.25
O(1)	.430	.319	.25
O(2)	.764	.319	.25
O(3)	.764	.653	.25
O(4)	.208	.542	.25
O(5)	.208	.875	.25
O(6)	.542	.875	.25

qualitative visual estimates of photographic intensities, it is hard to attach much significance to this argument. In several instances unexpectedly short interatomic distances have been ascribed to hydrogen bonds rather than to errors or inaccuracies in parameter determinations. It should be pointed out that, except with certain especially favorable crystals (such as the alkali acid fluorides), intensity data better than the usual qualitative estimates on simple reflections are needed to fix parameters with enough certainty to provide real evidence for such bonds.

Chapter XVIA. Structures of the Type $R_x(MX_4)_y$

(ac) The unimolecular tetragonal cell of β - Ag_2HgI_4 has atoms in the following special positions of V_d^1 (Figure 304a and b):

$$\begin{array}{ll} \text{Hg: (a) } 000 & \text{Ag: (f) } 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2} \\ \text{I: (n) } uuv; u\bar{u}\bar{v}; \bar{u}u\bar{v}; \bar{u}\bar{u}v \text{ with } u=0.27, v=0.225. \end{array}$$

The form of Cu_2HgI_4 stable at room temperature has the same structure with $u=0.255, v=0.275$.

(ad) The α -modification of Ag_2HgI_4 , stable above 50°C , is said to be truly cubic. The arrangement in the low temperature form (ac) is a distortion of the ZnS structure; this α -structure is described as an exact ZnS grouping [XI, (c)] with three-fourths of the positions (4b) $000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$ occupied by an irregular distribution of Hg+2 Ag.

The α -form of Cu_2HgI_4 , stable above 70°C , is like the silver salt.

(ae) Three studies have been made of the structure of anhydrous sodium sulfate, Na_2SO_4 . They agree in choosing an eight-molecule unit and in selecting V_h^{24} as corresponding space group. The atomic arrange-

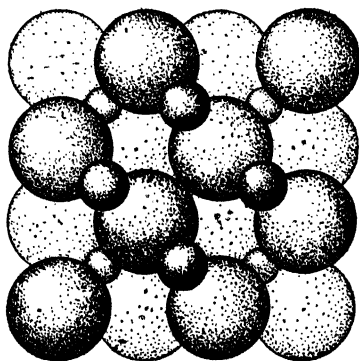
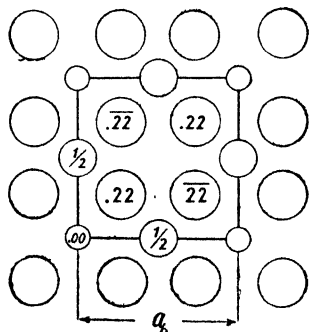


FIG. 304a.—(left) A c-face projection of atoms of the room temperature (β) modification of Ag_2HgI_4 . Atoms of I are represented by the largest, of Hg by the smallest circles.

FIG. 304b.—(right) A packing drawing of a with the atoms given their usual ionic sizes.

TABLE I. THE CRYSTAL STRUCTURES OF THE COMPOUNDS $R_x(MX_4)_y$

Substance, symmetry and structure type			a_o	c_o or α	References
β -Ag ₂ HgI ₄	Tetragonal	Ag ₂ HgI ₄ (<i>ac</i>)	6.340	6.340	1931, 257.
α -Ag ₂ HgI ₄ (stable above 50° C)	Cubic	(<i>ad</i>)	6.383		1934, 133.
AgIO ₄	Tetragonal	CaWO ₄ (<i>d</i>)	5.368	12.013	1932, 51.
AgReO ₄	Tetragonal	CaWO ₄ (<i>d</i>)	5.349	11.916	1933, 81.
Ag ₂ SO ₄	Ortho- rhombic	Na ₂ SO ₄ (<i>ae</i>)	5.847	10.251	1931, 179; 1932, 492.
Ag ₃ SbS ₄ (Stephanite)	Ortho- rhombic	(<i>af</i>)	7.85	8.58	1932, 394.
Ag ₂ SeO ₄	Ortho- rhombic	Na ₂ SO ₄ (<i>ae</i>)	6.069	10.211	1931, 179.
BAso ₄	Tetragonal	BPO ₄ (<i>ag</i>)	4.459	6.796	1933, 421; 1934, 240.
BPO ₄	Tetragonal	BPO ₄ (<i>ag</i>)	4.334	6.636	1933, 421; 1934, 240.
BaWO ₄	Tetragonal	CaWO ₄ (<i>d</i>), (<i>ah</i>)	5.64	12.70	1931, 344; 1932, 247.
BeNaPO ₄ (Beryllonite)	Monoclinic	(<i>ba</i>)	8.13	14.17	1934, 86.
CaCrO ₄	Tetragonal	ZrSiO ₄ (<i>f</i>), (<i>ai</i>)	7.25	6.34	1930, 381; 1932, 106.
Ca(F, Cl)Ca ₄ (PO ₄) ₃ (Apatite)	Hexagonal	(<i>aj</i>)			1930, 426; 1931, 298, 380; 1932, 203.
CaMg(OH)AsO ₄ (Adelite)	Ortho- rhombic	(<i>ay</i>)	5.88	7.43	1933, 7.
CaMg(OH)AsO ₄ (Tilasite)	Monoclinic	(<i>ay</i>)	5.68	7.57	1933, 7.
CdCr ₂ S ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	10.190		1931, 347.
CdFe ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.45		1931, 116.
CoAl ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.101		1931, 269; 1932, 30.
(Co, Ni) ₃ S ₄ (Linneite)	Cubic	MgAl ₂ O ₄ (<i>k</i>)	9.41 (for several minerals)		1931, 318.
CoSO ₄	Ortho- rhombic*		4.65	8.45	1931, 209.
Co ₂ TiO ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.420		1930, 246c; 1931, 212.
CsOsNO ₃	Ortho- rhombic	(<i>al</i>)	8.08	7.22	1932, 239, 241.
CsReO ₄	Ortho- rhombic	(<i>am</i>)	5.73	14.26	1933, 222.
Cs ₂ S ₂ O ₈	Monoclinic	(<i>bb</i>)	8.13	6.46	1934, 306.
CuAl ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.064 †		1931, 269; 1932, 223.
Cu ₃ AsS ₄ (Enargite)	Ortho- rhombic	(<i>an</i>)	6.46	6.18	1933, 463; 1934, 208.
CuFe ₂ O ₄ (quenched)	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)			1934, 281.

* This unit contains four molecules.

† The other determination (1931, 269) gives $a_o = 8.074 \text{ \AA}$.

Substance, symmetry and structure type		a_o	c_o or α	References
CuFe ₂ O ₄ (annealed)	Tetragonal (ak)	8.28	8.68	1934, 281.
Cu ₂ FeSnS ₄ (Stannite)	Tetragonal (bd)	5.46	10.725	1923, 64; 1934, 318.
β -Cu ₂ HgI ₄	Tetragonal Ag ₂ HgI ₄ (ac)	6.08	6.135	1931, 257.
α -Cu ₂ HgI ₄ (stable above 70° C)	Cubic (ad)	6.103		1934, 133.
Cu ₃ VS ₄ (Sulvanite)	Cubic (u), (ao)	5.370		1933, 350.
FeAl ₂ O ₄	Cubic MgAl ₂ O ₄ (k), (ak)	8.119*		1931, 80, 269; 1932, 30.
FeCr ₂ O ₄	Cubic MgAl ₂ O ₄ (k)	8.344		1931, 80.
(Fe, Mg)Cr ₂ O ₄ (Chromite)	Cubic MgAl ₂ O ₄ (k), (ap)			1932, 104.
Fe ₃ O ₄ (Magnetite)	Cubic MgAl ₂ O ₄ (k), (aq)	8.374		1931, 80; 1932, 345; 1934, 77.
Fe ₂ TiO ₄	Cubic MgAl ₂ O ₄ (k), (ak)	8.50		1932, 30.
FeV ₂ O ₄	Cubic MgAl ₂ O ₄ (k)			1932, 302.
Ga ₂ ZnO ₄	Cubic MgAl ₂ O ₄ (k)	8.323		1931, 75.
KBF ₄	Ortho- rhombic BaSO ₄ (a)	7.84	7.38	1930, 436.
KClO ₄ (low)	Ortho- rhombic BaSO ₄ (a), (ar)	8.834	b _o =5.68	1931, 404; 1932, 177.
			b _o =5.650	
K ₂ CrO ₄	Ortho- rhombic K ₂ SO ₄ (m), (as)	5.92	7.61	1931, 88, 501.
			b _o =10.40	
K ₂ Mg ₂ (SO ₄) ₃ (Langbeinite)	Cubic (at)	9.96		1931, 134.
KMnO ₄	Ortho- rhombic BaSO ₄ (a), (ar)	9.09	7.41	1931, 306.
			b _o =5.72	
KOsNO ₃	Tetragonal CaWO ₄ (d), (ah)	5.65	13.08	1932, 240, 241.
Li(Fe, Mn)PO ₄ (Triphylite)	Ortho- rhombic (au)	4.67	6.00	1932, 175.
			b _o =10.34	
Li ₃ PO ₄	Ortho- rhombic (au)	4.86	6.07	1932, 495.
			b _o =10.26	
Li ₂ SO ₄	Monoclinic (av)	8.25	8.44	1932, 5a.
			b _o =4.95, $\beta=107^{\circ}54'$	
MgAl ₂ O ₄ (Spinel)	Cubic MgAl ₂ O ₄ (k), (ak)	8.059±	0.004	1931, 80, 286; 1932, 101, 165, 286; 1934, 51.
MgCr ₂ O ₄	Cubic MgAl ₂ O ₄ (k)	8.305		1931, 80.
MgFe ₂ O ₄	Cubic MgAl ₂ O ₄ (k), (ak)	8.366		1931, 33, 80, 270; 1932, 30.
MgGa ₂ O ₄	Cubic MgAl ₂ O ₄ (k), (ak)	8.279		1931, 33; 1932, 30, 198, 295.

* In 1931, 269, a_o=8.084 Å.

Substance, symmetry and structure type		a_o	c_o or α	References
MgIn ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.81	1932, 30.
Mg ₂ TiO ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.44	1931, 212; 1932, 30.
MnAl ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.271	1931, 80, 269; 1932, 30.
MnCr ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.436	1931, 80.
MnCr ₂ S ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	10.045	1931, 347.
MnFe ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.457	1931, 80.
Mn ₂ TiO ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.67	1931, 212.
(NH ₄) ₂ BeF ₄	Ortho- rhombic	K ₂ SO ₄ (<i>m</i>), (<i>as</i>)	5.8 b _o =10.2	7.5 1934, 114.
NH ₄ ClO ₄ (low)	Ortho- rhombic	BaSO ₄ (<i>a</i>), (<i>ar</i>)	9.202 b _o =5.816	7.449 1931, 404; 1932, 177.
(NH ₄) ₂ CrO ₄	Monoclinic	(<i>aw</i>)	6.15 b _o =6.27, $\beta=115^\circ 13'$	7.66 1931, 73.
NH ₄ OsNO ₃	Ortho- rhombic	(<i>ax</i>)	5.53 b _o =5.86	13.54 1932, 238, 241.
(NH ₄) ₂ S ₂ O ₈	Monoclinic	(<i>bb</i>)	7.83 b _o =8.04, $\beta=95^\circ 9'$	6.13 1934, 306.
Na ₂ SO ₄	Ortho- rhombic	Na ₂ SO ₄ (<i>r</i>), (<i>ae</i>)	5.85 b _o =12.29	9.75 1931, 87; 1932, 493.
NiAl ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.050	1931, 269; 1932, 30.
NiCr ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.30	1932, 224.
Pb ₁₀ Cl ₂ (AsO ₄) ₆ (Mimetite)	Hexagonal	(<i>aj</i>)		1932, 203.
Pb ₁₀ Cl ₂ (PO ₄) ₆ (Pyromorphite)	Hexagonal	(<i>aj</i>)		1932, 203.
Pb ₁₀ Cl ₂ (VO ₄) ₆ (Vanadinite)	Hexagonal	(<i>aj</i>)		1932, 203.
PbCrO ₄ (Krokoite)	Monoclinic	(<i>i</i>)	7.10 b _o =7.40, $\beta=102^\circ 27'$	6.80 1931, 63.
PbZn(OH)VO ₄ (Descloizite)	Ortho- rhombic	(<i>az</i>)	6.05 b _o =9.39	7.56 1933, 24.
RbOsNO ₃	Ortho- rhombic	(<i>ax</i>)	5.57 b _o =5.84	13.64 1932, 238, 241.
RbReO ₄	Tetragonal	CaWO ₄ (<i>d</i>)	5.80	13.17 1933, 222.
TlOsNO ₃	Ortho- rhombic	(<i>ax</i>)	5.42 b _o =5.68	13.45 1932, 238, 241.
TlReO ₄	Ortho- rhombic	(<i>am</i>)	5.63 b _o =5.80	13.33 1932, 222.
YVO ₄	Tetragonal	ZrSiO ₄ (<i>f</i>)	7.126 6.197	1933, 75.
ZnAl ₂ O ₄	Cubic*	MgAl ₂ O ₄ (<i>k</i>), (<i>ak</i>)	8.062	1931, 80, 269; 1932, 30, 165, 198.
ZnCr ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.296	1931, 80.
ZnCr ₂ S ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	9.92	1931, 318.
ZnFe ₂ O ₄	Cubic	MgAl ₂ O ₄ (<i>k</i>)	8.423	1931, 80.

* In 1931, 269 and 1932, 198, $a_o=8.093$ A.

Substance, symmetry and structure type	a_o	c_o or α	References
ZnSO ₄ Orthorhombic (bc)	8.58	4.76 $b_o=6.73$	1934, 237.
Zn ₂ SnO ₄ Cubic MgAl ₂ O ₄ (k), (ak)	8.61		1932, 30.
Zn ₂ TiO ₄ Cubic MgAl ₂ O ₄ (k)	8.410		1930, 246c; 1931, 212.

ments proposed in the first two investigations are obviously wrong since they are chemically unreasonable, give unsatisfactory interatomic distances and fail to agree with observed intensities of reflection. The most recent structure (1932, 493), illustrated in Figure 305a and b, meets these requirements, the data being drawn from spectral photographs. Transferring the origin of 1930, 352, p. 69 to a center of symmetry at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, atoms are in the following positions:

- 8 S: (a) $\pm(\frac{1}{8}\frac{1}{8}\frac{1}{8})$ and 6 similar points about $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$ and $0\frac{1}{2}0$
- 16 Na: (g) $\pm(\frac{1}{8}\frac{1}{8}u)$; $\pm(\frac{1}{8}, \frac{1}{8}, \frac{1}{4}-u)$ and 12 similar points about $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}$ with $u=0.436$
- 32 O: (h) $\pm(xyz)$; $\pm(x, \frac{1}{4}-y, \frac{1}{4}-z)$; $\pm(\frac{1}{4}-x, y, \frac{1}{4}-z)$; $\pm(\frac{1}{4}-x, \frac{1}{4}-y, z)$ and 24 similar points about $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}$ with $x=-0.022, y=0.056, z=0.214$.

Silver sulfate, Ag₂SO₄, and the corresponding selenate, Ag₂SeO₄, are isomorphous with Na₂SO₄. The structure given them from a study of their photographic reflections is not like that outlined above and yields improbable interatomic distances. It has since been shown that these data are explicable in terms of the Na₂SO₄ structure with the following slightly different parameters for Ag₂SO₄: $u(\text{Ag})=0.450, x=0.022, y=0.058, z=0.208$.

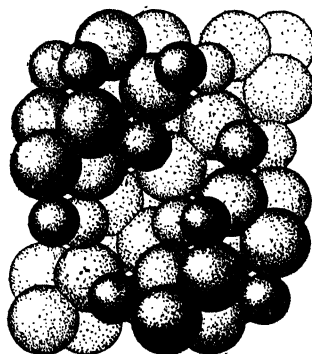
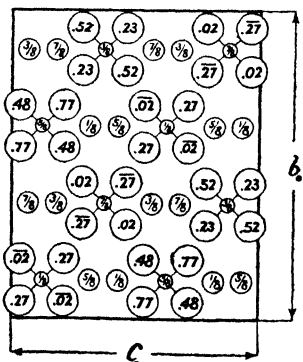


FIG. 305a.—(left) Atoms in the orthorhombic arrangement found for Na₂SO₄ projected on an a-face. The atoms forming the SO₄ ions are joined by light lines.

FIG. 305b.—(right) A packing drawing of the Na⁺ and SO₄⁻ ions in Na₂SO₄.

(af) The cell of **stephanite**, Ag_5SbS_4 , contains four molecules; its space group is said to be V_h^{17} .

(ag) The tetragonal cells of BPO_4 and BaSO_4 are bimolecular. According to a structure developed from S_4^2 they have atoms in the following positions:

B: (c) $0\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}0\frac{3}{4}$

P (or As): (a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

O: (g) xyz ; $\bar{y}\bar{x}\bar{z}$; $\bar{x}\bar{y}z$; $y\bar{x}\bar{z}$;

$x+\frac{1}{2}$, $y+\frac{1}{2}$, $z+\frac{1}{2}$; $\frac{1}{2}-y$, $x+\frac{1}{2}$, $\frac{1}{2}-z$; $\frac{1}{2}-x$, $\frac{1}{2}-y$, $z+\frac{1}{2}$; $y+\frac{1}{2}$, $\frac{1}{2}-x$, $\frac{1}{2}-z$.

For BPO_4 , $x=0.138$, $y=0.260$, $z=0.131$; for BaSO_4 , $x=0.160$, $y=0.260$, $z=0.140$. This arrangement, as a distortion of the high cristobalite grouping [XII, (ae), (bd)], consists of linked BO_4 and P (or As) O_4 tetrahedra (Figure 306a and b).

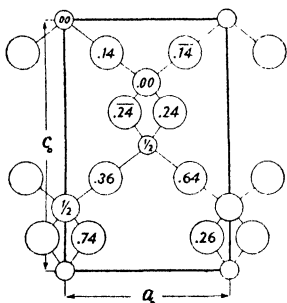


FIG. 306a.—(left) Atoms of the structure chosen for BPO_4 projected on one of the a -faces of its tetragonal cell. The smallest circles are P, the intermediate circles B atoms.

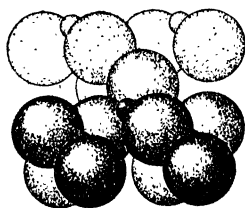


FIG. 306b.—(right) A packing drawing of a . The O atoms have their ionic radius; the size of the B atom is without significance.

(ah) Every study of crystals with the CaWO_4 (d) arrangement has resulted in different oxygen parameters. A new set, for BaWO_4 , is $x=0.20$, $y=0.46$, $z=0.32$.

Potassium osmiumate, KOsNO_3 , is reported to have this structure with N and O atoms indistinguishable from one another. The parameters chosen for these atoms are $x=0.23$, $y=0.05$, $z=-0.065$.

(ai) The positions found for the oxygen atoms in CaCrO_4 are those established in other crystals having the zircon grouping (f): $u=0.17$, $v=0.34$.

(aj) X-ray measurements have been made upon a number of substances with structures like apatite, $\text{Ca}(\text{F}, \text{Cl})\text{Ca}_4(\text{PO}_4)_3$, (z). The hexagonal unit prisms found in this way are recorded in Table II.

In the apatite arrangement (z) fluorine atoms are in (a) $00\frac{1}{2}$; $00\frac{3}{2}$. Another possible pair of positions, which could not be rigorously excluded by the observed intensities, would place them in the larger holes (b) 000 ; $00\frac{1}{2}$. It has been shown that in the lead compounds, $\text{Pb}_{10}\text{Cl}_2(\text{MO}_4)_6$, where $M=\text{P}$ or As , packing requires that the chlorine atoms must be in

these alternative positions (b). Parameters chosen to give suitable packing throughout the structure for these two crystals and for the chlor-X-apatite of Table II are listed in Table III. The previously found values for apatite itself are included for comparison.

TABLE II. UNIT CELLS OF APATITE-LIKE SUBSTANCES

Name	Formula	a_0	c_0
Apatite	$Ca_{10}(F, Cl)_2(PO_4)_6$	9.36	6.85
Chlor-X-Apatite	$Ca_{10}(Cl, X)_2(PO_4)_6$	9.52	6.85
Pyromorphite	$Pb_{10}Cl_2(PO_4)_6$	9.95	7.31
		9.95	7.32
Mimetite	$Pb_{10}Cl_2(AsO_4)_6$	10.24	7.43
		10.36	7.52
		10.31	7.34
Vanadinite	$Pb_{10}Cl_2(VO_4)_6$	10.47	7.43
Hydroxy-Apatite	$Ca_{10}(OH)_2(PO_4)_6$	9.40	6.93
Tricalcium Phosphate Hydrate	$Ca_3(H_2O)_2(PO_4)_6$	9.25	6.88
Oxy-Apatite	$Ca_{10}O(PO_4)_6$	9.38	6.93
Bone (Naphtha extracted)		9.27	6.95

TABLE III. PARAMETERS IN APATITE AND RELATED CRYSTALS

Atom	Apatite			Pyromorphite			Mimetite			Chlor-X-Apatite		
	x	y	z	x	y	z	x	y	z	x	y	z
F, Cl	0	0	$\frac{1}{2}$	0	0	0	0	0	0	0	0	0
Ca, Pb(1) (f)	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0
Ca, Pb(2) (h)	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.003	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$
P, As (h)	0.416	0.361	$\frac{1}{2}$	0.417	.369	$\frac{1}{2}$	0.411	0.392	$\frac{1}{2}$	0.417	0.361	$\frac{1}{2}$
O(1) (h)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$.344	.480	$\frac{1}{2}$.317	.458	$\frac{1}{2}$.333	.500	$\frac{1}{2}$
O(2) (h)	.60	.466	$\frac{1}{2}$.600	.464	$\frac{1}{2}$.644	.503	$\frac{1}{2}$.600	.467	$\frac{1}{2}$
O(3)	$\frac{1}{2}$	$\frac{1}{2}$	0.062	.350	.250	0.063	.336	.272	0.061	.333	.250	0.063

(ak) Unexpected intensities are observed from a number of compounds which obviously have the spinel, $MgAl_2O_4$, structure (k). Two explanations have been offered: one is that the metal atoms are distributed haphazardly among all the metal positions, both (8f) and (16c); the other considers that half of the sixteen chemically alike atoms are in (8f) and that the rest together with the eight chemically alike metal atoms are irregularly distributed throughout (16c). The latter has been called an "equipoint" structure. Qualitative estimates of intensity do not seem to conflict with the second interpretation but more quantitative observations and calculations are needed for final confirmation. Accurate parameters have been found for the oxygen atoms in several compounds. These additional data are collected in Table IV.

Cupric ferrite, $CuFe_2O_4$, when quenched, is cubic with the spinel structure; if it is slowly cooled or annealed at $350^\circ C$ for some time its pattern is said to be that of the tetragonal cell of Table I.

THE STRUCTURE OF CRYSTALS

TABLE IV. TYPE AND PARAMETER FOUND FOR SEVERAL SPINEL STRUCTURES

<i>Normal</i>	<i>Type</i>	<i>Parameter</i>
	"Equipoint"	<i>u</i>
CoAl ₂ O ₄		0.390
FeAl ₂ O ₄		.390
	FeTiFeO ₄	.390
MgAl ₂ O ₄		.390
	FeMgFeO ₄	.390
	GaMgGaO ₄	.392
	InMgInO ₄	.372
	MgTiMgO ₄	.390
MnAl ₂ O ₄		.390
NiAl ₂ O ₄		.390
ZnAl ₂ O ₄		.390
	ZnSnZnO ₄	.390

(al) The unit prism of CsOsNO₃ contains four molecules. Its Cs and Os atoms are said to be in the following positions of V²:

$$\text{Os: (c) } 0u\frac{1}{4}; 0\bar{u}\frac{3}{4} \text{ and (d) } \frac{1}{2}u'\frac{1}{4}; \frac{1}{2}\bar{u}'\frac{3}{4} \text{ with } u=u'=\frac{1}{8}$$

$$\text{Cs: (e) } xyz; x\bar{y}\bar{z}; \bar{x}, y, \frac{1}{2}-z; \bar{x}, \bar{y}, z+\frac{1}{2} \text{ with } x=\frac{1}{4}, y=\frac{5}{8}, z=\frac{1}{4}.$$

(am) Four molecules are included in the pseudo-tetragonal orthorhombic cells of CsReO₄ and TlReO₄. The space group has been given as V_h¹⁶.

(an) Two differing determinations have been made of the structure of enargite, Cu₃AsS₄. According to one the atoms of its single molecule cell are all in positions (g) of the orthorhombic space group V_h¹². Sulfur atoms are in one set of these special positions, copper and arsenic atoms, grouped together, in another.

The unit prism of the other and presumably correct arrangement (see Table I) is twice as high in the direction of the b-axis, i.e. b_o=7.43 Å. The atoms in the bimolecular unit are distributed according to the following cases of C_{2v}⁷:

$$(a) u0v; \bar{u}, \frac{1}{2}, v+\frac{1}{2} \quad (b) xyz; \bar{x}, \frac{1}{2}-y, z+\frac{1}{2}; \bar{x}, y+\frac{1}{2}, z+\frac{1}{2}; x\bar{y}z$$

with the parameters listed in Table V. The axes of this description differ from those of 1930, 352 by an interchange of X' and Y'. Like so many

TABLE V. PARAMETERS OF THE ATOMS IN Cu₃AsS₄

<i>Atom</i>	<i>No. per cell</i>	<i>Positions</i>	<i>x</i>	<i>y</i>	<i>z</i>
As	2	(a)	0.820	0	0
Cu(1)	2	(a)	.165	0	0.500
Cu(2)	4	(b)	.333	0.245	.990
S(1)	2	(a)	.830	0	.360
S(2)	2	(a)	.140	0	.875
S(3)	4	(b)	.330	.255	.367

other sulfides this grouping is a system of sulfur tetrahedra linked by sharing corners and having metal atoms at their centers. As Figure 307b shows, the packing is excellent if the crystal is assumed to be made up of neutral atoms (As-S=2.21 Å, Cu-S=2.31 Å).

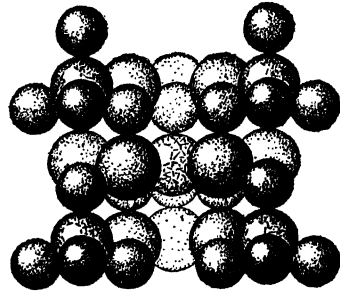
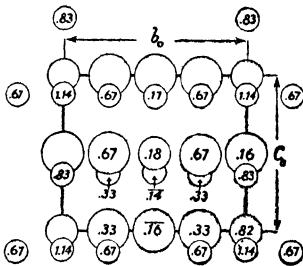
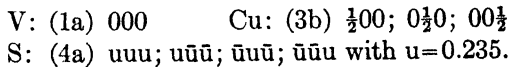


FIG. 307a.—(left) The orthorhombic unit of enargite, Cu_3AsS_4 , projected on its a -face. The small circles are S, the largest circles are Cu atoms.

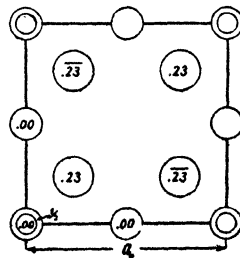
FIG. 307b.—(right) A packing drawing of Cu_3AsS_4 giving the atoms their neutral radii. Atoms of As are line-shaded.

(ao) A new and simpler structure has been found for **sulvanite, Cu_3VS_4** . With a cube edge half that previously chosen, the unimolecular cell has atoms in the following positions of T_d^1 (Figure 308):



This leads to a V-S separation of 2.18 Å; the Cu-S distance is 2.28 Å.

FIG. 308.—A cube face projection of the atoms in the new grouping established for sulvanite, Cu_3VS_4 . The smallest circles are V, the largest S atoms.



(ap) The edge lengths of the unit cube of several chromites, (Fe, Mg) $(\text{Cr, Al})_2\text{O}_4$, have been measured. These lengths increase with the Cr_2O_3 content.

(aq) Powder photographs of magnetite, Fe_3O_4 , made at various temperatures down to ca -170°C prove that the anomalous heat effect found

at -160° C is not due to a change in structure. Like MnO , Fe_2O_3 is, however, reported to have a region in which it shrinks on being warmed (see Table II, Chapter XIA).

(ar) Positions have been assigned to all the atoms in three substances, KMnO_4 , KClO_4 and NH_4ClO_4 , with the barite, BaSO_4 , structure (a). These crystals have units which are almost identical in size and it is probable that their real atomic positions are practically the same. Nevertheless the structures proposed for the permanganate and for the perchlorates show important differences (Figures 309 and 310). The KMnO_4 determination rests on photographic spectral data; the observations on KClO_4 and NH_4ClO_4 are more quantitative spectrometric measurements. It is, however, difficult to be sure of the deductions from the latter results. The published parameters are obviously wrong: they correspond to an utterly impossible grouping. If the drawing of the perchlorate paper (1932, 177) is assumed to be correct and the parameters are altered to fit it, a structure is obtained which yields the interatomic distances stated in the paper and which therefore is probably the intended one. These parameters, and the values for KMnO_4 expressed in terms of a unit with

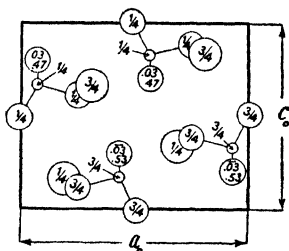


FIG. 309.—(left) The unit cell of the orthorhombic structure found for KMnO_4 projected on its b-face. Atoms of the MnO_4 ions are connected by light lines.

FIG. 310.—(right) The arrangement selected for KClO_4 projected upon its b-face. Atoms of the ClO_4 tetrahedra are united by light lines.

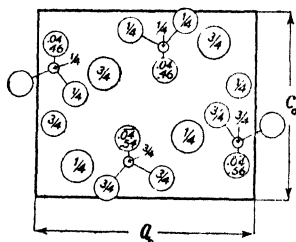


TABLE VI. PARAMETERS OF THE ATOMS IN KMnO_4 , KClO_4 AND NH_4ClO_4

Atom	Positions	KMnO_4			KClO_4^*			$\text{NH}_4\text{ClO}_4^*$		
		x	y	z	x	y	z	x	y	z
K or NH_4	(c)	0.19	$\frac{1}{2}$	0.16	0.192	$\frac{1}{2}$	0.167	0.197	$\frac{1}{2}$	0.172
Mn or Cl	(c)	.07	$\frac{1}{2}$.67	.075	$\frac{1}{2}$.689	.067	$\frac{1}{2}$.694
O(1)	(c)	.99	$\frac{1}{2}$.49	.175	$\frac{1}{2}$.550	.169	$\frac{1}{2}$.550
O(2)	(c)	.25	$\frac{1}{2}$.61	-.078	$\frac{1}{2}$.606	-.078	$\frac{1}{2}$.600
O(3)	(d)	.07	0.03	.80	.083	0.042	.819	.075	0.042	.819

* These values are obtained from the parameters of 1932, 177 by adding $\frac{1}{2}$ to the z coordinates of Cl, O(1) and O(2), and by changing the sign of x of O(2) and z of O(3).

the same origin, are listed in Table VI. The necessary coordinates (as stated on p. 283 of book) are:

$$(c) \pm(u\frac{1}{4}v); \pm(u+\frac{1}{2}, \frac{1}{4}, \frac{1}{2}-v)$$

$$(d) \pm(xyz); \pm(x, \frac{1}{2}-y, z); \pm(x+\frac{1}{2}, y, \frac{1}{2}-z); \pm(x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z).$$

It is interesting that in spite of the very different positions of atoms O(1) and O(2), neither of these arrangements gives unreasonable atomic separations and each is supposed to be required by the observed data. Additional work will undoubtedly provide another demonstration of the fact that acceptable interatomic distances and qualitative agreement with a limited number of intensity estimations are insufficient to establish most structures with many parameters.

(as) Atomic positions have been found in two crystals isomorphous with K_2SO_4 (*m*)— K_2CrO_4 and $(NH_4)_2BeF_4$. Their parameters (Table VII) are essentially those previously chosen for the alkali sulfates. The values recorded for K_2CrO_4 in Table VII have been derived from the conclusions of 1931, 501 by reversing the signs along *c* and adding one half.

TABLE VII. PARAMETERS OF THE ATOMS IN K_2CrO_4 AND $(NH_4)_2BeF_4$

Atom	No. per cell	For K_2CrO_4			Atom	For $(NH_4)_2BeF_4$		
		<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
K(1)	4	$\frac{1}{2}$	0.417	0.644	NH ₄ (1)	$\frac{1}{2}$	0.393	0.675
K(2)	4	$\frac{1}{2}$	-.305	0	NH ₄ (2)	$\frac{1}{2}$	-.325	-.046
Cr	4	$\frac{1}{2}$.417	.230	Be	$\frac{1}{2}$.417	.263
O(1)	4	$\frac{1}{2}$.417	.019	F(1)	$\frac{1}{2}$.390	.051
O(2)	4	$\frac{1}{2}$.561	.300	F(2)	$\frac{1}{2}$.573	.300
O(3)	8	0.028	.345	.300	F(3)	0.024	.353	.350

(at) The unit cube of $K_2Mg_2(SO_4)_3$ contains four molecules. Its space group has been found to be T^4 .

(au) The mineral **triphylite**, $Li(Fe,Mn)PO_4$, and the compound Li_3PO_4 have orthorhombic cells similar in size and shape to the unit of chrysoberyl, $BeAl_2O_4$, (*l*). It has been inferred that their structures too are similar.

(av) The monoclinic unit of Li_2SO_4 contains four molecules. An arrangement, based on spectral photographs, places all its atoms in the general positions (e) $\pm(xyz); \pm(\frac{1}{2}-x, y+\frac{1}{2}, z)$ of C_{2h}^6 . The chosen parameters, recorded in Table VIII, give the grouping illustrated in Figure 311.

(aw) The monoclinic cell of $(NH_4)_2CrO_4$ is bimolecular. The space group is reported to be C_1^1 .

(ax) **Ammonium osmiumate**, NH_4OsNO_3 , like $CsReO_4$ (*am*), has a four-molecule pseudo-tetragonal orthorhombic unit suggesting the tetragonal $CaWO_4$ (*d*) arrangement. The space group assigned to NH_4OsNO_3 , V^4 , is different from that proposed for $CsReO_4$.

The rubidium and thallium salts, RbOsNO_3 and TlOsNO_3 , are structurally isomorphous with NH_4OsNO_3 . It is thought that the rubidium and osmium atoms in the general positions of V^4 , xyz ; $x+\frac{1}{2}$, $\frac{1}{2}-y$, \bar{z} ; \bar{x} , $y+\frac{1}{2}$, $\frac{1}{2}-z$; $\frac{1}{2}-x$, \bar{y} , $z+\frac{1}{2}$, have as approximate parameters, for Rb: $x=0.03$, $y=\frac{1}{4}$, $z=\frac{5}{8}$; for Os: $x=0.03$, $y=\frac{1}{4}$, $z=\frac{1}{8}$.

TABLE VIII. PARAMETERS OF THE ATOMS IN Li_2SO_4

Atom	x	y	z
Li(1)	0.205	0.582	0.375
Li(2)	.455	.582	.125
S	.319	.061	.250
O(1)	.492	-.042	.250
O(2)	.186	-.042	.099
O(3)	.280	-.042	.401
O(4)	.319	.367	.250

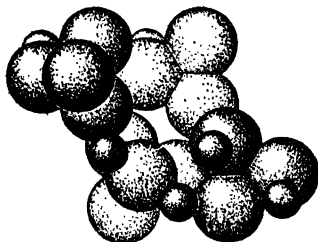
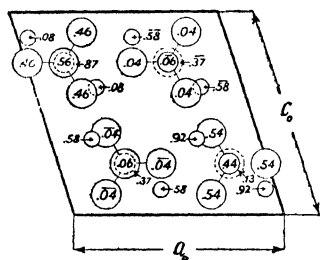


FIG. 311a.—(left) The monoclinic structure determined for Li_2SO_4 projected on its b -face. The largest circles are O, the smallest are Li atoms.

FIG. 311b.—(right) A packing drawing of a showing Li ions and SO_4 tetrahedra.

(ay) Two minerals, **adelite** and **tilasite**, each of which is essentially $\text{CaMg}(\text{OH})\text{AsO}_4$, have units similar in shape and size though the first is orthorhombic, the latter monoclinic. Both cells contain four molecules.

(az) The space group of **descloizite**, $\text{PbZn}(\text{OH})\text{VO}_4$, has been fixed as V_h^{16} ; its cell includes four molecules. The following minerals are said to be isomorphous, with Cu sometimes replacing some Zn: **cuprodescloizite**, **mottramite**, **psittacinite**, **chileite**, **eusynchite** and **dechinite**.

(ba) The mineral **beryllonite** is orthorhombic both in its crystallography and its X-ray data. The optical anomalies it shows have, however, been considered to be sufficiently marked to prove its monoclinic symmetry. For such a crystal the 12-molecule cell of the table is without doubt too large to be the true unit.

(bb) The monoclinic cell of ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, is bimolecular. From Laue and spectral photographs it has been concluded that the space group is C_{2h}^5 with all atoms in the general positions (e) $\pm(xyz); \pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$ [see p. 58]. The chosen atomic parameters are listed in Table IX. As can be seen from Figure 312a and b, this determination yields an S_2O_8 ion which consists of two SO_4 tetrahedra joined through an oxygen-to-oxygen bond (O-O=1.46 Å).

The cesium analogue, $\text{Cs}_2\text{S}_2\text{O}_8$, is isomorphous. Cesium parameters have been taken as $x=0.144$, $y=0.125$, $z=0.228$; the parameters for the other atoms have the same values as in the ammonium salt.

TABLE IX. PARAMETERS OF THE ATOMS IN $(\text{NH}_4)_2\text{S}_2\text{O}_8$

Atom	x	y	z
NH_4	0.144	0.125	0.250
S	.136	.350	.708
O(1)	.042	.500	.611
O(2)	.028	.194	.680
O(3)	.208	.417	.930
O(4)	.292	.347	.597

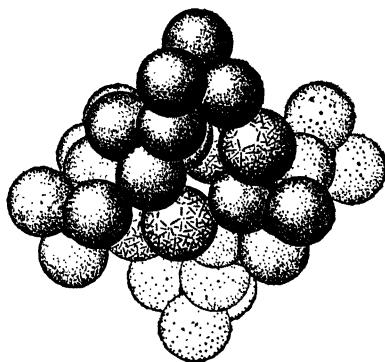
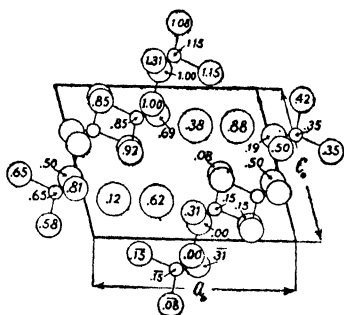


FIG. 312a.—(left) The monoclinic arrangement found for $(\text{NH}_4)_2\text{S}_2\text{O}_8$ projected on its b -face. The largest circles are NH_4 ions; the atoms of S_2O_8 ions are connected by light lines.

FIG. 312b.—(right) A packing drawing of a . The NH_4 ions are linc-shaded.

(bc) Four molecules are to be found in the unit prism of anhydrous ZnSO_4 . Its space group has not yet been established.

(bd) The sulfide mineral stannite, $\text{Cu}_2\text{FeSnS}_4$, has a tetragonal two-molecule unit. Photographic data have placed its atoms in the following special positions of V_d^{11} :

Fe: (a) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ Sn: (b) $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$ Cu: (d) $\frac{1}{2}0\frac{1}{4}$; $\frac{1}{2}0\frac{3}{4}$; $0\frac{1}{2}\frac{1}{4}$; $0\frac{1}{2}\frac{3}{4}$ S: (i) uuv ; $u\bar{u}\bar{v}$; $\bar{u}u\bar{v}$; $\bar{u}u\bar{v}$

and four similar positions about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Like most other sulfides this structure for stannite (Figure 312c and d) can be considered as an assemblage of tetrahedra with sulfur at their centers. The interatomic distances that prevail are Cu-S=2.31 Å, Sn-S=2.43 Å, Fe-S=2.36 Å. Of these the iron-sulfur separation is exceptionally large.

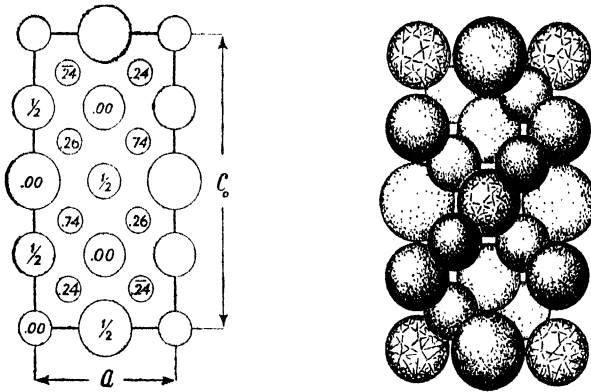


FIG. 312c.—(left) The tetragonal structure found for stannite, $\text{Cu}_2\text{FeSnS}_4$, projected on an a-face. Atoms of Sn, Cu, Fe and S are represented by circles of decreasing size.

FIG. 312d.—(right) A packing drawing of c in which atoms have their neutral radii. Atoms of Fe are line-shaded.

Chapter XVIII. Structures of the Type $R_x(MX_6)_y$

(j) A number of compounds isomorphous with $Ba_2Ni(NO_2)_6$ are reported to be cubic and to have the $(NH_4)_2PtCl_6$ structure (a). A more detailed study of one or more of these crystals is needed to insure that the symmetry really is cubic and to establish the positions of the nitrogen and oxygen atoms.

(k) Several complex nitrites isomorphous with $Cs_3Rh(NO_2)_6$ are said to be cubic. Their atomic arrangements are considered to be like that of $(NH_4)_3FeF_6$ (g) with nitrogen in place of fluorine and oxygen in positions (48f) $u\bar{u}0$; etc. (1930, 352, p. 113). For several of these crystals $u(N)$ has been chosen as 0.26, $u'(O)$ as 0.13. Such a distribution is improbable since it would cause the oxygen atoms to be shared between neighboring nitrogen atoms instead of forming distinct NO_2 groups.

(l) The unit cubes of $Ca_3[Al(OH)_6]_2$ and of $Sr_3[Al(OH)_6]_2$ have been described as containing eight molecules; their space groups are given as O_h^{10} .

(m) The unit cubes of the **alkali fluophosphates** isomorphous with KPF_6 contain four molecules. Their space group is thought to be T^2 and it is asserted that the observed intensities conflict with the idea of PF_6 radicals. Further work is obviously needed before anything is known about the structures of these crystals.

(n) The bromine parameter in K_2SeBr_6 has been determined as 0.245; in $(NH_4)_2SeBr_6$ it lies between 0.24 and 0.25. It has been stated that for all similar compounds listed in Table I, $u(Cl)$ is greater than 0.23 and less than 0.25.

(o) The compound NaK_2AlF_6 has been given a structure which is a slight distortion of the $(NH_4)_3FeF_6$ arrangement (g). Aluminum atoms are at (4b) 000; etc., Na at (4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; etc. The potassium atoms are in (8h) with a parameter $u=0.25$ thus making their positions identical with (8e) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; etc. The fluorine atoms are put in general positions (d) xyz ; etc. of T_h^6 (see p. 268 of book) with $x=0.03$, $y=0.01$, $z=0.22$. No data have been published which allow an estimate of the accuracy of this determination.

TABLE I. THE CRYSTAL STRUCTURES OF THE COMPOUNDS $R_x(MX_6)_y$

Substance, symmetry and structure type		a_0	c_0 or α	References
$Ba_2Ni(NO_2)_6$	Cubic (j)	10.67		1933, 135.
$Ba_3[Rh(NO_2)_6]_2$	Cubic or Pseudo-cubic (r)	10.70		1933, 134.
$Ca_3[Al(OH)_6]_2$	Cubic (l)	12.56		1933, 70.
$Cs_2AgAuCl_6$	Cubic (s)	5.33		1934, 78.
$Cs_2Au^+Au^{+++}Cl_6$	Cubic (s)	5.33		1934, 78.
$Cs_3Co(NO_2)_6$	Cubic (k)	11.15		1933, 133.
$Cs_3Fe(CN)_6$	(e)			1931, 314.
$Cs_3Ir(NO_2)_6$	Cubic (k)	11.17		1933, 132.
$CsPF_6$	Cubic (m)	8.19		1931, 407, 408.
Cs_2PbCl_6	Cubic $(NH_4)_2PtCl_6$	10.415		1933, 126; 1934, 325.
	(a), (n)			
Cs_2PtCl_6	Cubic $(NH_4)_2PtCl_6$	10.185*		1932, 325; 1933, 54, 126; 1934, 325.
	(a), (n)			
$Cs_3Rh(NO_2)_6$	Cubic (k)	11.30		1933, 134.
Cs_2SeCl_6	Cubic $(NH_4)_2PtCl_6$	10.260		1934, 325.
	(a), (n)			
Cs_2SnCl_6	Cubic $(NH_4)_2PtCl_6$	10.348		1933, 126; 1934, 325.
	(a), (n)			
Cs_2TeCl_6	Cubic $(NH_4)_2PtCl_6$	10.449		1932, 326; 1933, 126; 1934, 325.
	(a), (n)			
Cs_2TiCl_6	Cubic $(NH_4)_2PtCl_6$	10.219		1934, 325.
	(a), (n)			
Cs_2ZrCl_6	Cubic $(NH_4)_2PtCl_6$	10.407		1934, 325.
	(a), (n)			
$K_2BaCo(NO_2)_6$	Cubic (f)	10.45		1931, 111.
$K_2BaNi(NO_2)_6$	Cubic (f)	10.67		1931, 111.
$K_2CaCo(NO_2)_6$	Cubic (f)	10.17		1931, 111.
$K_2CaNi(NO_2)_6$	Cubic (f)	10.29		1931, 111.
$K_3Co(NO_2)_6$	Cubic (?) (k)	10.44		1931, 111a; 1933, 133.
$K_3Cr(CN)_6$	(d)			1931, 314.
$K_3Fe(CN)_6$	(d)			1931, 314; 1933, 83.
$K_3Ir(CN)_6$	(d)			1931, 314.
$K_3Ir(NO_2)_6$	Cubic (k)	10.57		1933, 132.
$K_3Mn(CN)_6$	(d)			1931, 314.
K_2NaAlF_6	Cubic (o)	8.69		1932, 311.
$K_4Ni(NO_2)_6$	Cubic (?) (p)	10.49		1931, 111a.
K_2OsNCl_6 †				1933, 483.
$K_3OsO_2Cl_4$	Tetragonal (q)	6.99	8.75	1934, 109.
KPF_6	Cubic (m)	7.76		1931, 407, 408.
K_2PtCl_6	Cubic $(NH_4)_2PtCl_6$	9.725		1934, 325.
	(a), (n)			
$K_3Rh(NO_2)_6$	Cubic (k)	10.63		1933, 134.
K_3SeBr_6	Cubic $(NH_4)_2PtCl_6$	10.363		1933, 200.
	(a), (n)			

* According to 1933, 54, $a_0 = 10.120$ A.

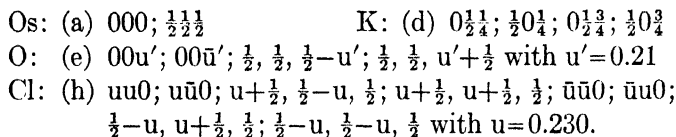
† Journal not available.

Substance, symmetry and structure type		a_0	c_0 or α	References
K_2SnCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.983	1934, 325.
$K_2SrCo(NO_2)_6$	Cubic	(f)	10.23	1931, 111.
$K_2SrNi(NO_2)_6$	Cubic	(f)	10.49	1931, 111.
K_2TeCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.143	1934, 325.
$(NH_4)_3Co(NO_2)_6$	Cubic	(k)	10.81	1933, 133.
$(NH_4)_3CrF_6$	Cubic	(g)	9.01	1932, 356.
$(NH_4)_3Ir(NO_2)_6$	Cubic	(k)	10.73	1933, 132.
NH_4PF_6	Cubic	(m)	7.92	1931, 407, 408.
$(NH_4)_2PbCl_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.135	1934, 325.
$(NH_4)_2PtCl_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.834	1934, 325.
$(NH_4)_3Rh(NO_2)_6$	Cubic	(k)	10.91	1933, 134.
$(NH_4)_2SeBr_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.46	1932, 425.
$(NH_4)_2SeCl_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.935	1934, 325.
$(NH_4)_2SiF_6$	Hexagonal	(t)	5.76	4.77 1934, 87.
$(NH_4)_2SnCl_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.038	1934, 325.
$(NH_4)_2TeCl_6$	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.178	1934, 325.
$(NH_4)_3VF_6$	Cubic	(g)	9.04	1932, 355.
N_3AlF_6		(h)		1932, 311.
$Pb_2Ni(NO_2)_6$	Cubic	(j)	10.55	1933, 135.
$Pb_3[Rh(NO_2)_6]_2$	Cubic or Pseudo-cubic	(r)	10.53	1933, 134.
$Rb_3Co(NO_2)_6$	Cubic	(k)	10.73	1933, 133.
$Rb_3Fe(CN)_6$	Monoclinic	$K_3Fe(CN)_6$ (d)	13.74 $b_0=10.66, \beta=90^\circ 3'$	8.63 1933, 83.
$Rb_3Ir(NO_2)_6$	Cubic	(k)	10.77	1933, 132.
Rb_2PbCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.198	1933, 126; 1934, 325.
Rb_2PtCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.882	1932, 325; 1933, 54. 126; 1934, 325.
$Rb_3Rh(NO_2)_6$	Cubic	(k)	10.83	1933, 134.
Rb_2SeCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.978	1934, 325.
Rb_2SnCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.100	1933, 126; 1934, 325.
Rb_2TeCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.233	1933, 126; 1934, 325.
Rb_2TiCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	9.922	1934, 325.
Rb_2ZrCl_6	Cubic	$(NH_4)_2PtCl_6$ (a), (n)	10.178	1934, 325.
$Sr_3[Al(OH)_6]_2$	Cubic	(l)	13.02	1933, 70.
$Sr_2Ni(NO_2)_6$	Cubic	(j)	10.54	1933, 135.
$Tl_3Co(NO_2)_6$	Cubic	(k)	10.72	1933, 133.

Substance, symmetry and structure type		a_0	c_0 or α	References
$Tl_3Ir(NO_2)_6$	Cubic (k)	10.73		1933, 132.
Tl_2PtCl_6	Cubic (a), (n)	$(NH_4)_2PtCl_6$ 9.755		1934, 325.
$Tl_3Rh(NO_2)_6$	Cubic (k)	10.91		1933, 134.
Tl_2SiF_6	Cubic (a)	$(NH_4)_2PtCl_6$ 8.60		1933, 460.
Tl_2SnCl_6	Cubic (a), (n)	$(NH_4)_2PtCl_6$ 9.970		1934, 325.
Tl_2TeCl_6	Cubic (a), (n)	$(NH_4)_2PtCl_6$ 10.107		1934, 325.

(p) The compound $K_4Ni(NO_2)_6$, which probably has less than cubic symmetry, has been given a cubic or pseudo-cubic unit containing four molecules.

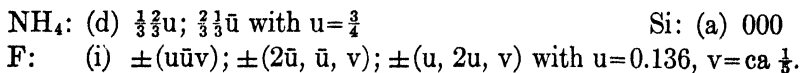
(q) The tetragonal unit of potassium osmyl chloride, $K_2OsO_2Cl_4$, is bimolecular. Its atoms, with an arrangement which is a slight distortion of the familiar $(NH_4)_2PtCl_6$ grouping (a), are in the following special positions of D_{4h}^{17} :



(r) Unit cubes or pseudo-cubes of $Ba_3[Rh(NO_2)_6]_2$ and $Pb_3[Rh(NO_2)_6]_2$ are supposed to contain two molecules.

(s) Powder patterns obtained from the triple halides $Cs_2AgAuCl_6$ and $Cs_2Au^+Au^{+++}Cl_6$ have only the lines required by a perovskite, $CaTiO_3$ [XV, (d)], arrangement. Such a unit would contain only half a molecule; hence it is suggested that the atoms have as coordinates: Cs: 000, Cl: $0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0$, Ag (or Au^+) and Au^{+++} at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in different cells. Though the structure probably approaches such a simple atomic distribution, the true unit undoubtedly is a larger one.

(t) The unit prism established for the hexagonal modification of $(NH_4)_2SiF_6$ is unimolecular. A structure has been proposed which places atoms in the following special positions of D_{3d}^3 :



Practically no data have been published in support of this arrangement.

Chapter XVIIIA. Structures of Hydrates and Ammoniates and of Miscellaneous Inorganic Compounds

Hydrates and Ammoniates

The hydrates thus far analyzed by X-ray methods fall into three types. Most of them, and all of the ammoniates, are coordination compounds in which the H_2O or NH_3 molecules are closely bound to the metal atoms present. In a few of the crystals described below water molecules are not thus associated with cations but occupy holes in the lattice. Such a water molecule is present in $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ (*ba*); the fifth H_2O in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is similarly held. Though these H_2O molecules cannot be driven off without destroying the rest of the atomic arrangement, in many other ways their bonding resembles that seen in the zeolites. To the third type belong those compounds, like $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, with water so firmly held that it may be present as hydroxyl groups. Many minerals contain such "water of constitution."

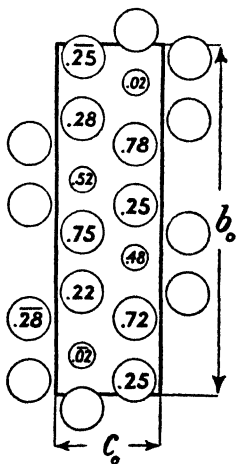


FIG. 313a.—(left) A portion of the disaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, structure projected on an *a*-face. Small circles are Al atoms. Water molecules, as such, do not exist in this grouping.

FIG. 313b.—(right) A packing drawing of *a*.

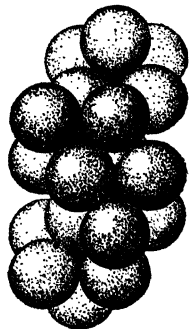


TABLE I. THE CRYSTAL STRUCTURES OF HYDRATES AND AMMONIATES

Substance, symmetry and structure type			a_o	c_o or α	References
$Al_2O_3 \cdot H_2O$ (Diaspore)	Ortho- rhombic	$Al_2O_3 \cdot H_2O$ (<i>a</i>), (<i>ae</i>)	4.43	2.80 $b_o=9.36$	1932, 121; 1933, 462.
$CaCrO_4 \cdot H_2O$	Ortho- rhombic	(<i>af</i>)	7.99	8.11 $b_o=12.77$	1932, 106.
$2(CaSO_4) \cdot ca H_2O$	Hexagonal	(<i>ag</i>)	6.76	6.24	1934, 46.
$Fe_2O_3 \cdot H_2O$ (Goethite)	Ortho- rhombic	$Al_2O_3 \cdot H_2O$ (<i>a</i>), (<i>ae</i>)	4.64	3.03 $b_o=10.0$	1931, 132; 1932, 168.
$Fe_2O_3 \cdot H_2O$ (Lepidocrocite)	Ortho- rhombic	(<i>ae</i>)	3.87	3.06 $b_o=12.4$	1931, 132.
$3(KPbCl_3) \cdot H_2O$	Triclinic		14.35	14.50* $b_o=9.05$	1934, 172.
$Li_2SO_4 \cdot H_2O$	Monoclinic	(<i>br</i>)	5.43	8.14 $b_o=4.83, \beta=107^\circ 35'$	1934, 361.
$Mn_2O_3 \cdot H_2O$ (Manganite)	Ortho- rhombic	(<i>ah</i>)	4.41	2.83 $b_o=5.19$	1931, 112.
$Na_2CO_3 \cdot H_2O$	Ortho- rhombic	(<i>bs</i>)	10.72	5.24 $b_o=6.44$	1934, 321.
$Rb_2(CrF_6 \cdot H_2O)$	Cubic	$(NH_4)_2PtCl_6$ (<i>m</i>)	8.38		1932, 356.
$Sb_2O_4 \cdot H_2O$ (Stibiconite)	Cubic	(<i>ai</i>)	10.24		1933, 316.
$Tl_2(VF_6 \cdot H_2O)$	Cubic	$(NH_4)_2PtCl_6$ (<i>m</i>)	8.45		1932, 355.
$AgNO_3 \cdot 2NH_3$	Ortho- rhombic	(<i>bt</i>)	8.00	6.29 $b_o=10.58$	1934, 58.
$CaCrO_4 \cdot 2H_2O$	Ortho- rhombic	(<i>aj</i>)	16.02	5.60 $b_o=11.39$	1932, 106.
$CaHPO_4 \cdot 2H_2O$ (Brushite)	Monoclinic	(<i>ak</i>)	10.47	6.28 $b_o=15.15, \beta=98^\circ 58'$	1931, 149.
$CaSO_4 \cdot 2H_2O$ (Gypsum)	Monoclinic	(<i>d</i>), (<i>ak</i>)			1931, 149; 1934, 347a.
$Cd(ClO_2)_2 \cdot 2H_2O$	Monoclinic	(<i>al</i>)	8.86	9.76 $b_o=7.12, \beta=90^\circ 18'$	1931, 282.
$K_2CuCl_4 \cdot 2H_2O$	Tetragonal	(<i>e</i>), (<i>am</i>)			1934, 48.
$(NH_4)_2CuBr_4 \cdot 2H_2O$	Tetragonal	$(NH_4)_2CuCl_4 \cdot 2H_2O$ (<i>e</i>), (<i>am</i>)	7.83	8.14	1933, 370.
$(NH_4)_2CuCl_4 \cdot 2H_2O$	Tetragonal	(<i>e</i>), (<i>am</i>)			1934, 48.
$NaBr \cdot 2H_2O$	Monoclinic	(<i>an</i>)	6.59	6.51 $b_o=10.20, \beta=112^\circ 30'$	1932, 482.
$NaI \cdot 2H_2O$	Triclinic	(<i>ao</i>)	6.85	7.16 $b_o=5.76, \alpha=98^\circ, \beta=119^\circ, \gamma=68\frac{1}{2}^\circ$	1932, 482.
α -Pt $(NH_3)_2Cl_4$	Tetragonal	(<i>ap</i>)	5.72	10.37	1933, 109.
β -Pt $(NH_3)_2Cl_4$	Ortho- rhombic	(<i>ap</i>)	10.0	6.0 $b_o=11.2$	1933, 109.

* For $3(KPbCl_3) \cdot H_2O$, $\alpha=\gamma=ca 90^\circ$, $\beta=113^\circ$.

Substance, symmetry and structure type			a_0	c_0 or α	References
Zn(ClO ₂) ₂ ·2H ₂ O	Monoclinic	(al)	8.67	9.38	1931, 282.
			$b_0 = 6.88$, $\beta = 90^\circ 20'$		
Al ₂ O ₃ ·3H ₂ O (Gibbsite)	Monoclinic	(aq)	8.6236	9.699	1934, 170.
			$b_0 = 5.0602$, $\beta = 85^\circ 26'$		
Ba(ClO ₄) ₂ ·3H ₂ O	Hexagonal	(bq)	7.28	9.64	1934, 290.
LiClO ₄ ·3H ₂ O	Hexagonal	(bp)	7.71	5.42	1934, 290.
LiI·3H ₂ O	Hexagonal	(f), (bp)			1934, 290.
Ag ₂ SO ₄ ·4NH ₃	Tetragonal	(ar)	8.43	6.35	1934, 59.
BaNi(CN) ₄ ·4H ₂ O	Monoclinic	(as)	11.71	6.63	1934, 32, 33.
			$b_0 = 13.48$, $\beta = 104^\circ 50'$		
BaPt(CN) ₄ ·4H ₂ O	Monoclinic	(as)	11.89	6.54	1933, 72.
			$b_0 = 14.08$, $\beta = 103^\circ 42'$		
BaSO ₄ ·4H ₂ O	Tetragonal	(h), (at)	8.02	10.75	1931, 401; 1932, 31.
[Co ^{CO} _{(NH₃)₄]ClO₄}	Ortho- rhombic	(au)	18.05	6.95	1933, 455.
			$b_0 = 8.10$		
1, 6[Co ^{(NO₂)₂} _{(NH₃)₄]Cl}	Ortho- rhombic	(av)	14.36	13.98	1933, 456.
			$b_0 = 17.97$		
Na ₂ B ₄ O ₇ ·4H ₂ O (Kernite)	Monoclinic	(aw)	15.65	7.01	1932, 156, 157.
			$b_0 = 9.07$, $\beta = 108^\circ 52'$		
[Pt(NH ₃) ₄]PtCl ₄ (Magnus' Green Salt)	Tetragonal	(ax)	6.297	6.42 †	1931, 193; 1932, 119.
[Pt(NH ₃) ₄]PtCl ₄ (Magnus' Red Salt)		(ax)			1931, 193; 1932, 119.
Zn(ClO ₄) ₂ ·4NH ₃	Cubic	(ay)	10.250		1933, 53.
CuSO ₄ ·5H ₂ O	Triclinic	(i), (az)	5.12	5.97	1933, 32; 1934, 15, 15a.
			$b_0 = 10.7$, $\alpha = 82^\circ 16'$, $\beta = 107^\circ 26'$, $\gamma = 102^\circ 40'$		
H ₃ PW ₁₂ O ₄₀ ·5H ₂ O	Cubic	(bk)	12.14		1934, 131.
Pd(NH ₃) ₄ Cl ₂ ·H ₂ O	Tetragonal	(ba)	10.302	4.34	1933, 109; 1934, 71.
Pt(NH ₃) ₄ Cl ₂ ·H ₂ O	Tetragonal	(ba)	10.44	4.21	1932, 114; 1933, 109.
AlCl ₃ ·6H ₂ O	Hexagonal	(bb)	7.85	$97^\circ \pm 20'$	1934, 3.
BaI ₂ ·6H ₂ O	Hexagonal	SrCl ₂ ·6H ₂ O (p)	8.90	4.60	1931, 185.
CaBr ₂ ·6H ₂ O	Hexagonal	SrCl ₂ ·6H ₂ O (p)	7.97	3.97	1931, 184.
CaBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (m)	10.706		1933, 56.
CaCl ₂ ·6H ₂ O	Hexagonal	SrCl ₂ ·6H ₂ O (p)	7.86	3.905	1931, 184.
CaI ₂ ·6H ₂ O	Hexagonal	SrCl ₂ ·6H ₂ O (p)	8.4	4.25	1931, 185.
CaI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (m)	11.24		1933, 56.
Cd(BF ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (m)	11.380		1933, 54.
CdBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (m)	11.540		1933, 56.

† In 1931, 193, $c_0 = 5.15$ A.

Substance, symmetry and structure type		a_o	c_o or α	References
Cd(ClO ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.588	1933, 53.
CdI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.046	1933, 53.
Cd(SO ₃ F) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.619	1933, 54.
CdSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>)	9.35 6.27 $b_o=12.705, \beta=106^\circ 41'$	1931, 211.
[Co·6NH ₃](BF ₄) ₂	Cubic	(<i>m</i>)	11.265	1932, 195; 1933, 54.
[Co·6NH ₃](BF ₄) ₃	Cubic	(NH ₄) ₃ FeF ₆ (<i>l</i>)	11.211	1933, 53.
[Co·6NH ₃]Br ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.389	1933, 55.
[Co·6NH ₃]Cl ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.10	1933, 55.
[Co·6NH ₃](ClO ₄) ₂	Cubic	(<i>m</i>)	11.449	1932, 195.
[Co·6NH ₃](ClO ₄) ₃	Cubic	(<i>l</i>)	11.384	1932, 195.
[Co·6NH ₃]I ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.914	1933, 55.
[Co·6(NH ₂ ·CH ₃)]I ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	12.05	1933, 55.
[Co·6NH ₃](PF ₆) ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.942	1933, 53.
[Co·6NH ₃](PF ₆) ₃	Cubic	(NH ₄) ₃ FeF ₆ (<i>l</i>)	11.670	1933, 53.
[Co·6NH ₃](SO ₃ F) ₂	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.490	1933, 54.
CoSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>)	9.23 6.23 $b_o=12.49, \beta=106^\circ 56'$	1931, 150.
CrCl ₃ ·6H ₂ O	Hexagonal	(<i>bb</i>)	7.95 $97^\circ \pm 20'$	1934, 3.
Fe(BF ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.340	1933, 54.
FeBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.468	1933, 53.
FeCl ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.148	1933, 53.
Fe(ClO ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.517	1933, 53.
FeI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.965	1933, 53.
Fe(SO ₃ F) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.544	1933, 54.
FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>), (<i>bc</i>)	9.28 6.22 $b_o=12.57, \beta=106^\circ 50'$	1931, 211.
Mg(BF ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.337	1933, 54.

Substance, symmetry and structure type			a_0	c_0 or α	References
MgBr ₂ ·6H ₂ O	Monoclinic	(<i>bd</i>)	10.25	6.30	1934, 4.
			$b_0=7.40, \beta=93^\circ30'$		
MgBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.468		1933, 53.
MgCl ₂ ·6H ₂ O	Monoclinic	(<i>bd</i>)	9.90	6.10	1934, 4.
			$b_0=7.15, \beta=94^\circ\pm20'$		
MgCl ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.158		1933, 53.
Mg(ClO ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.531		1933, 53.
MgI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.978		1933, 53.
MgSO ₄ ·K ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>)	9.04	6.095	1931, 211.
			$b_0=12.24, \beta=104^\circ48'$		
MgNH ₄ AsO ₄ ·6H ₂ O	Orthorhombic	(<i>bo</i>)	7.00	11.14	1933, 397.
			$b_0=6.14$		
MgSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>), (<i>bc</i>)	9.28	6.20	1931, 211; 1932, 220.
			$b_0=12.57, \beta=107^\circ6'$		
MgSeO ₄ ·(NH ₄) ₂ SeO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>)	9.42	6.30	1931, 211.
			$b_0=12.72, \beta=106^\circ27'$		
MgSO ₄ ·Ti ₂ SO ₄ ·6H ₂ O	Monoclinic	(<i>n</i>)	9.22	6.185	1931, 211.
			$b_0=12.42, \beta=106^\circ30'$		
Mn(BF ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.374		1933, 54.
MnBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.519		1933, 53.
MnCl ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.198		1933, 53.
Mn(ClO ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.578		1933, 53.
MnI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.037		1933, 53.
Mn(SO ₃ F) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.593		1933, 54.
Ni(BF ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.219		1932, 195; 1933, 54.
NiBr ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.34		1933, 55.
NiCl ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.064		1933, 55.
Ni(ClO ₄) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.410		1932, 195.
NiI ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	10.875		1933, 55.
NiI ₂ ·6(NH ₂ CH ₃)	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	12.027		1933, 55.
Ni(PF ₆) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.912		1933, 53.
Ni(SO ₃ F) ₂ ·6NH ₃	Cubic	(NH ₄) ₂ PtCl ₆ (<i>m</i>)	11.445		1932, 195; 1933, 54.

Substance, symmetry and structure type		a_o	c_o or α	References
NiSO ₄ ·6H ₂ O	Tetragonal (be)	6.80	18.3	1932, 32; 1933, 102.
SrBr ₂ ·6H ₂ O	Hexagonal SrCl ₂ ·6H ₂ O	8.212	4.146	1931, 183.
	(p)			
SrCl ₂ ·6H ₂ O	Hexagonal SrCl ₂ ·6H ₂ O	7.906	4.07	1931, 185.
	(p), (bf)			
SrI ₂ ·6H ₂ O	Hexagonal SrCl ₂ ·6H ₂ O	8.51	4.29	1931, 184.
	(p)			
ZnBr ₂ ·6NH ₃	Cubic (NH ₄) ₂ PtCl ₆	10.46		1933, 56.
	(m)			
ZnI ₂ ·6NH ₃	Cubic (NH ₄) ₂ PtCl ₆	10.964		1933, 53.
	(m)			
ZnSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	(n)	9.205	6.225	1931, 211.
	Monoclinic	$b_o=12.475$, $\beta=106^\circ52'$		
[Co ^{CO₃} (NH ₃) ₄] ₂ SO ₄ ·3H ₂ O	(bn)	11.80	7.42	1933, 454.
	Monoclinic	$b_o=10.60$, $\beta=98^\circ39'$		
MgPt(CN) ₄ ·7H ₂ O	(t), (bg)	14.6	6.26	1932, 60.
	Tetragonal			
MgSO ₄ ·7H ₂ O	Orthorhombic			1930, 378; 1932, 19.
3CdSO ₄ ·8H ₂ O	Monoclinic (bh)	14.65	16.35	1932, 138.
		$b_o=11.84$, $\beta=34^\circ48'$		
SrO ₂ ·8H ₂ O	Tetragonal (v), (bi)			1932, 322.
Na ₃ SbS ₄ ·9H ₂ O	Cubic*			1933, 483.
4(PO ₄)Al·2Al(OH) ₃ ·9H ₂ O	(bl)	7.27	10.80	1933, 225.
(Wavellite)	Orthorhombic	$b_o=14.41$		
Zn ₁₄ (AsO ₄) ₉ OH·12H ₂ O	(bm)	12.70	10.18	1932, 130.
(Legrandite)	Monoclinic	$b_o=7.90$, $\beta=75^\circ35'$		
2Na ₃ PO ₄ ·NaF·19H ₂ O	(bj)	27.86		1933, 322.
	Cubic			
GdPMo ₁₂ O ₄₀ ·30H ₂ O	(bk)	23.1		1933, 198.
	Cubic			
H ₃ PMo ₁₂ O ₄₀ ·30H ₂ O	(bk)	23.281		1933, 198, 248, 249.
	Cubic			
NdPMo ₁₂ O ₄₀ ·30H ₂ O	(bk)	23.10		1933, 198.
	Cubic			
SaPMo ₁₂ O ₄₀ ·30H ₂ O	(bk)	23.1		1933, 198.
	Cubic			
Be ₂ SiW ₁₂ O ₄₀ ·31H ₂ O	(bk)	23.3		1933, 198.
	Cubic			
Mg ₂ SiMo ₁₂ O ₄₀ ·31H ₂ O	(bk)	23.04		1933, 198.
	Cubic			
Ni ₂ SiMo ₁₂ O ₄₀ ·31H ₂ O	(bk)	23.0		1933, 198.
	Cubic			

* The journal describing this work was not available.

(ae) The orthorhombic units of **diaspore**, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{H}_2\text{Al}_2\text{O}_4$, and of goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, are bimolecular. Studied independently, they have been given identical arrangements. All atoms are in special positions (c) of V_h^{16} : $uv\frac{1}{4}$; $\bar{u}\bar{v}\frac{3}{4}$; $u+\frac{1}{2}$, $\frac{1}{2}-v$, $\frac{3}{4}$; $\frac{1}{2}-u$, $v+\frac{1}{2}$, $\frac{1}{4}$ with the values of u and v listed in Table II. Except for c_0 which is half as long, the units of these oxides and of chrysoberyl, BeAl_2O_4 , are similar in size and shape. As is readily seen by comparing Figure 313 with Figure 219 (book, p. 293) the two groupings are similar, both being packings of oxygen atoms with the small metal atoms lying in interstices.

The other monohydrate of Fe_2O_3 , lepidocrocite, also has a bimolecular orthorhombic unit but its space group is V_h^1 . It is said that lepidocrocite, unlike goethite, gives magnetic Fe_2O_3 on dehydration.

(af) The unit cell of $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ contains eight molecules. Its probable space group is V_h^{15} .

TABLE II. PARAMETERS OF THE ATOMS IN DIASPORE AND GOETHITE

Atom	For $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$		For $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	
	u	v	u	v
Al or Fe	-0.02	0.11	-0.05	0.103
O(1)	.75	-.04	.75	-.04
O(2)	.22	.29	.25	.29

(ag) Recent work on **plaster of Paris** revives the question of whether a hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, or anhydrous CaSO_4 provides the proper formula. It has been shown that the water remaining in burnt plaster can be nearly all removed without destroying the crystal form and without altering the diffraction pattern. From this it has been concluded that the water is present in a zeolitic condition—within holes existing in the crystalline structure. Assuming that plaster of Paris is built only of CaSO_4 molecules, three of them are to be found within the prism of Table I.

(ah) The unit cell selected for **manganite**, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, contains one molecule. Except for the fact that the length of the b-axis is halved, this cell is practically the same in size and shape as those of diaspore and goethite.

(ai) **Stibiconite**, $\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$, gives a powder pattern identical with that of the anhydrous tetroxide Sb_2O_4 . It is therefore not surprising that no change of pattern occurs on dehydration.

(aj) The unit prism of $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ contains eight molecules; its space group is described as V_h^{11} .

(ak) **Gypsum**, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, are said to have indistinguishable X-ray patterns and hence to possess unit cells of the same size and shape. It is reported that ardealite is a 1:1 double salt of these compounds with practically the same cell.

In a very recent study it is concluded that the correct space group of gypsum is C_{2h}^6 and not C_{2h}^3 upon which the structure described in (d) (book, p. 314) was based.

(al) Four molecules are found within the monoclinic units assigned to $Cd(ClO_2)_2 \cdot 2H_2O$ and $Zn(ClO_2)_2 \cdot 2H_2O$.

(am) Previous studies of crystals isomorphous with $(NH_4)_2CuCl_4 \cdot 2H_2O$ gave two different atomic arrangements. A reinvestigation, based on quantitative intensity data and Fourier plots of electron distributions, leads to a structure that differs from the first one described under (e) (book, p. 314) only in making equal the parameters u and v for the chlorine atoms in (f) and (g) [$u=v=0.220$] and in reducing the water parameters in (e) to $w=0.25$. This arrangement for $K_2CuCl_4 \cdot 2H_2O$ gives definitely better agreement with quantitative data than does the second one having chlorine atoms in (j). It is interesting that no choice between these arrangements could be made from the $(NH_4)_2CuCl_4 \cdot 2H_2O$ reflections.

(an) The monoclinic unit found for $NaBr \cdot 2H_2O$ contains four molecules; its space group is C_{2h}^5 .

(ao) The compound $NaI \cdot 2H_2O$ is described as triclinic with a two-molecule unit and with C_1^1 as space group.

(ap) The α -diamminoplatinic chloride is reported to be tetragonal with a two-molecule unit; its space group has been given as D_{4h}^{14} .

The β -form, of a lower symmetry, is said to have a four-molecule orthorhombic unit.

(aq) Making use of photographic data and some spectrometric measurements a pronouncedly layer-like structure has been assigned to gibbsite (hydrargillite), $Al_2O_3 \cdot 3H_2O$. Atoms of the 8 $Al(OH)_3$ molecules within the large monoclinic unit that has been used are in general positions of C_{2h}^5 : (e) $\pm(xyz)$; $\pm(\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z)$. The chosen atomic parameters are stated in Table III.

TABLE III. PARAMETERS OF THE ATOMS IN GIBBSITE, $Al_2O_3 \cdot 3H_2O$

Atom	x	y	z
Al(1)	0.177	0.520	-0.005
Al(2)	.333	.020	-.005
O(1)	.182	.202	-.110
O(2)	.682	.672	-.110
O(3)	.515	.132	-.110
O(4)	-.015	.632	-.110
O(5)	.298	.702	-.100
O(6)	.838	.172	-.100

(ar) The tetragonal unit of $Ag_2SO_4 \cdot 4NH_3$ contains two molecules. Its atoms are in the following special and general positions of V_4^4 :

S: (a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ Ag: (d) $0\frac{1}{2}u$; $\frac{1}{2}0\bar{u}$; $\frac{1}{2}$, 0 , $\frac{1}{2}-u$; 0 , $\frac{1}{2}$, $u+\frac{1}{2}$ with $u=0.50$
 O: (e) xyz ; $y\bar{x}\bar{z}$; $\bar{x}\bar{y}z$; $\bar{y}x\bar{z}$; $\frac{1}{2}-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$; $\frac{1}{2}-y$, $\frac{1}{2}-x$, $z+\frac{1}{2}$; $x+\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}-z$;
 $y+\frac{1}{2}$, $x+\frac{1}{2}$, $z+\frac{1}{2}$ with $x=0.14$, $y=0.07$, $z=0.15$
 NH₄: (e) $x'y'z'$; etc. with $x'=0.10$, $y'=0.30$, $z'=0.50$.

As Figure 314 shows, this arrangement is a packing of SO₄ tetrahedra and linear NH₃-Ag-NH₃ groups.

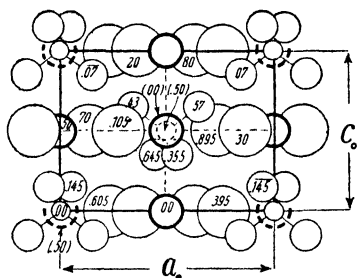


Fig. 314a.—(left) The structure of Ag₂SO₄·4NH₃ projected on one of the a-faces of its tetragonal unit. The largest circles are NH₃ groups, the smallest are S atoms; Ag atoms are shown as thick rings.

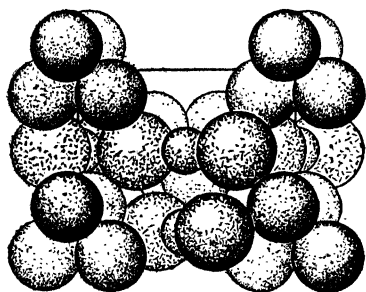


Fig. 314b.—(right) A packing drawing of *a*. The small Ag atoms and the large NH₃ groups are line-shaded.

(as) The monoclinic units assigned to BaNi(CN)₄·4H₂O and to the isomorphous BaPt(CN)₄·4H₂O contain four molecules. The space group is given as C_{2h}⁶ with Pt (or Ni) atoms at 000 ; $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and Ba atoms at $0\frac{3}{8}\frac{1}{4}$; $0\frac{5}{8}\frac{3}{4}$; $\frac{1}{2}\frac{1}{8}\frac{1}{4}$; $\frac{1}{2}\frac{7}{8}\frac{3}{4}$. Other atomic positions have not been fixed.

(at) Two determinations of the structure of BeSO₄·4H₂O have been made from photographic data. The first (1931, 401), based on D_{4h}⁸, is undoubtedly wrong. The other places atoms in the following positions of V_d¹⁰ (written not as the face-centered grouping of 1930, 352, p. 77 but in terms of a diagonal body-centered unit):

S: (c) $\frac{1}{2}00$; $0\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$ Be: (b) $00\frac{1}{4}$; $00\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{3}{4}$
 O: (i) xyz ; $y\bar{x}\bar{z}$; $\bar{x}\bar{y}z$; $\bar{y}x\bar{z}$; $x+\frac{1}{2}$, $\frac{1}{2}-y$, z ; $y+\frac{1}{2}$, $\frac{1}{2}-x$, \bar{z} ;
 $\frac{1}{2}-y$, $x+\frac{1}{2}$, \bar{z} ; $\frac{1}{2}-x$, $y+\frac{1}{2}$, z and 8 similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

For the sulfate oxygen atoms $x=0.40$, $y=0.13$, $z=0.08$. The water molecules, likewise in (i), are given the parameters $x'=0.10$, $y'=0.14$, $z'=0.16$.

In this arrangement the beryllium atoms, which of course cannot be located with certainty by the X-ray data, have been placed at the centers of the groups of water molecules. The structure as a whole thus is a packing together of SO₄ and Be(H₂O)₄ tetrahedra (Figure 315).

(au) The orthorhombic cell which has been given to [Co(CO₄)₂]₂ClO₄ contains four molecules. Its space group is said to be C_{2v}⁷.

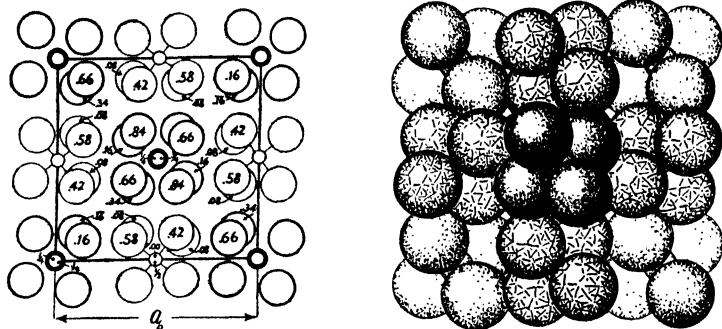


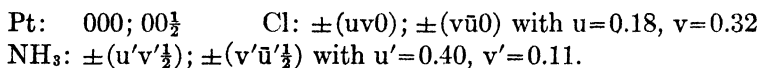
FIG. 315a.—(left) The atomic arrangement in tetragonal $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ projected on its c-face. Be atoms are shown as thick rings, S atoms as the smallest circles. The H_2O molecules are thickened large circles.

FIG. 315b.—(right) A packing drawing of *a*. Oxygens of the SO_4 tetrahedra are line-shaded; Be atoms show within their water tetrahedra.

(aw) The orthorhombic unit of $1,6[\text{Co}(\text{NO}(\text{NH}_3)_4)_2]\text{Cl}$ is reported to contain 16 molecules.

(aw) The unit found for $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ possesses four molecules; its space group is thought to be C_{2h}^4 .

(ax) The two studies that have been made of Magnus' green salt, $[\text{Pt}(\text{NH}_3)_4]\text{PtCl}_4$, do not agree in the height of its one-molecule tetragonal unit. The following atomic positions, suggested in 1932, 119, are not adequately established by the published data:



In 1931, 193 it is said that Magnus' red salt has not only the same composition as the green salt but a cell of similar size and shape ($a_0=6.293$ A, $c_0=5.25$ A). Another determination (1932, 119) concludes that it is orthorhombic with $a_0=7.9$ A, $b_0=8.2$ A, $c_0=7.9$ A.

(ay) The unit cube of $\text{Zn}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$ is said to contain four molecules. It would be interesting to establish, by further chemical analyses, that this salt is really a tetrammoniate and not a hexammoniate.

(az) A recent study of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, based on photographic data and a Fourier analysis of some spectrometric measurements, has led to an arrangement which places the copper atoms in its bimolecular triclinic unit in the symmetry centers 000 and $\frac{1}{2}\frac{1}{2}0$. The other atoms are in general positions $\pm(xyz)$ of C_i^1 with the parameters of Table IV.

As can be seen from Figure 316 the water molecules are of two kinds. Four of them are coordinated with the copper atoms. The fifth, like zeolitic water, occupies a hole in the structure, its neighbors being two

TABLE IV. PARAMETERS OF THE ATOMS IN $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Atom	No. per cell	x	y	z
Cu(1)	1	0	0	0
Cu(2)	1	$\frac{1}{2}$	$\frac{1}{2}$	0
S	2	0	0.28	0.64
O(1)	2	0.89	.15	.69
O(2)	2	.24	.31	.82
O(3)	2	.86	.38	.64
O(4)	2	.02	.30	.38
$\text{H}_2\text{O}(1)$	2	.83	.08	.16
$\text{H}_2\text{O}(2)$	2	.29	.11	.17
$\text{H}_2\text{O}(3)$	2	.48	.41	.32
$\text{H}_2\text{O}(4)$	2	.76	.42	.01
$\text{H}_2\text{O}(5)$	2	.43	.12	.65

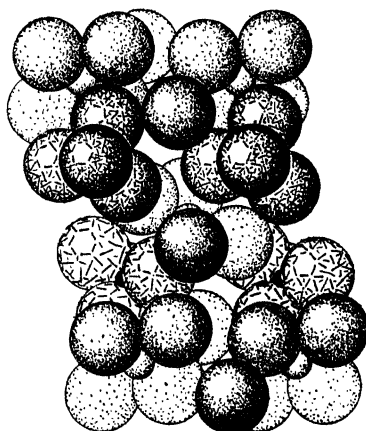
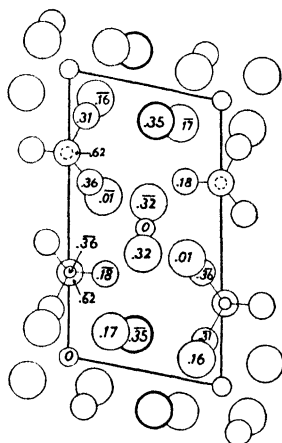


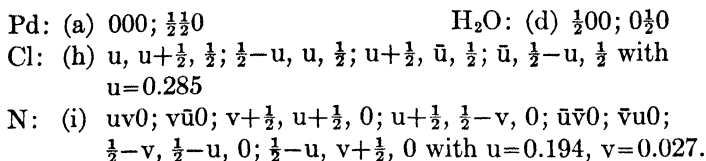
FIG. 316a.—(left) A projection of the triclinic $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ arrangement viewed down the c -axis (after 1934, 15a). The smallest circles are S atoms, the largest are H_2O molecules. Non-coordinated H_2O molecules are thickened. Atoms of the SO_4 ions are connected by light lines.

FIG. 316b.—(right) A packing drawing of *a*. The sulfate oxygens are line-shaded; small black S atoms show in two of the SO_4 groups. All H_2O molecules, whether coordinated with the Cu atoms or not, are dot-shaded.

water molecules and two sulfate oxygen atoms. Each copper atom is surrounded by an octahedron of atoms. Four of these are its coordinated water molecules situated approximately at the corners of a square, the other two, farther away, are oxygens from different sulfate groups.

(ba) Three unit cells have been suggested for $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and its platinum analogue. The small one-molecule and the large four-molecule prisms are presumably wrong. The most recent study (1934, 71),

using Laue and spectral photographic data, places the atoms of the two-molecule cells (Table I) in the following special positions of D_{4h}^5 :



Four coordinated NH_3 molecules are arranged about a central palladium atom at the corners of a square ($\text{NH}_3\text{-Pd}=2.02 \text{ \AA}$). The extent to which packing prevails in basal planes of this structure and the way the H_2O molecules lie in holes present in these planes can best be seen from Figure 317.

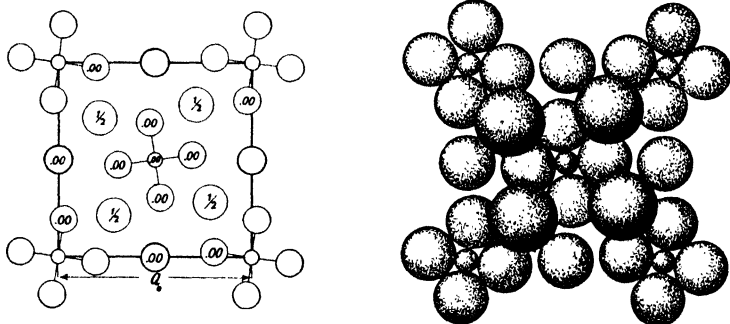
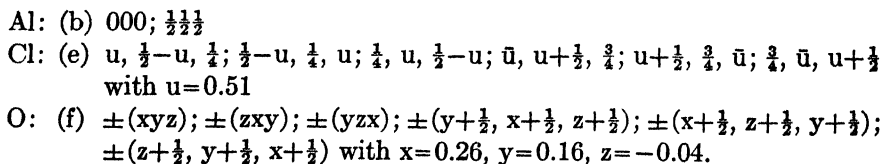


Fig. 317a.—(left) The atomic arrangement assigned to tetragonal $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ as projected on its c -face. The largest circles are Cl ions, the smallest are Pd atoms. Intermediate circles are NH_3 , if light in outline, H_2O if heavy.

Fig. 317b.—(right) A packing drawing of a . The H_2O and NH_3 molecules are not distinguished.

(bb) The rhombohedral unit found for $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and for the isomorphous $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, contains two molecules. An atomic arrangement of both salts, based on D_{3d}^6 , has been determined as:



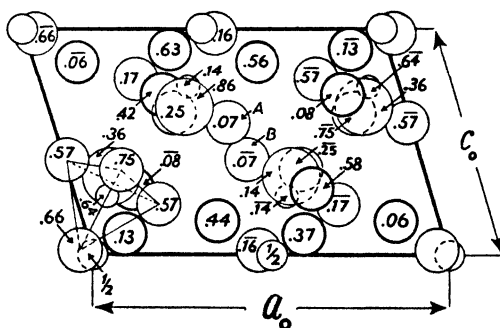
(bc) The two-molecule cells of $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and of the many crystals isomorphous with it have arrangements developed from

C_{2h}^5 . A structure deduced from an elaborate consideration of photographic data has all atoms except magnesium in the general positions: $(e) \pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$, with the parameters listed in Table V. Mg atoms are at $(a) 000; \frac{1}{2}\frac{1}{2}0$. This arrangement can scarcely be correct because while the NH_4 -O and Mg- H_2O separations are satisfactory, sulfate oxygens belonging to different SO_4 groups (such as A and B in Figure 318) are much too near together (O-O=ca 2.10 Å).

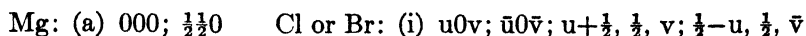
TABLE V. PARAMETERS OF THE ATOMS IN $MgSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Atom	x	y	z
NH_4	0.120	0.357	0.345
S	.090	.635	.260
O(1)	.153	.746	.376
O(2)	-.032	.656	.020
O(3)	.227	.566	.225
O(4)	.012	.571	.419
$H_2O(1)$.108	.127	.094
$H_2O(2)$.168	-.084	.290
$H_2O(3)$.123	-.062	-.150

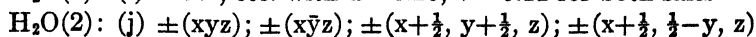
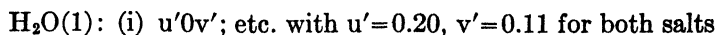
FIG. 318.—The unit cell of the structure proposed for $MgSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ as projected on its b-face. The smallest circles are S atoms, the largest NH_4 ions. Circles slightly larger than S are Mg ions. Molecules of H_2O are distinguished from sulfate O atoms by being heavily ringed.



(bd) The monoclinic units of $MgBr_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ contain two molecules. Photographic data have been used in choosing the following arrangement, based on C_{2h}^3 :



For Cl, $u=0.320$, $v=0.615$; for Br, $u=0.318$, $v=0.615$.



with $x=0.96$, $y=0.20$ for both salts, $z=0.230$ for the chloride and 0.225 for the bromide.

(be) The four molecules in the elongated tetragonal unit of $NiSO_4 \cdot 6H_2O$ are arranged according to the demands of the enantiomorphic pair

of space groups D_4^4 and D_4^8 . Expressed in terms of D_4^4 the atomic positions found for this crystal are:

Ni: (a) $uu0$; $\bar{u}\bar{u}\frac{1}{2}$; $u+\frac{1}{2}, \frac{1}{2}-u, \frac{3}{4}$; $\frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{4}$ with $u=0.71$

S: (a) $u'u'0$; etc. with $u'=0.21$

H_2O and O: (b) xyz ; $y+\frac{1}{2}, \frac{1}{2}-x, z+\frac{3}{4}$; $\bar{x}, \bar{y}, z+\frac{1}{2}$; $\frac{1}{2}-y, x+\frac{1}{2}, z+\frac{1}{4}$;
 $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{4}-z$; $\bar{y}, \bar{x}, \frac{1}{2}-z$; $x+\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4}-z$; $yx\bar{z}$

with the parameters of Table VI.

TABLE VI. PARAMETERS OF THE OXYGEN ATOMS IN $NiSO_4 \cdot 6H_2O$

Atom	x	y	z
O(1)	0.12	0.12	0.068
O(2)	.43	.17	.000
$H_2O(1)$.67	.45	.054
$H_2O(2)$.97	.75	.054
$H_2O(3)$.56	.86	.077

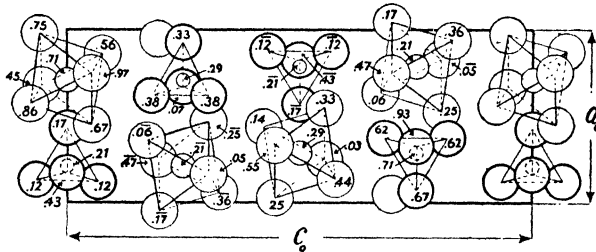


FIG. 319a.—A projection of the tetragonal $NiSO_4 \cdot 6H_2O$ grouping upon one of its a -faces. In this figure the sulfate oxygens are heavily ringed, the H_2O molecules lightly outlined. Medium sized circles, at the centers of the water octahedra, are the Ni atoms.

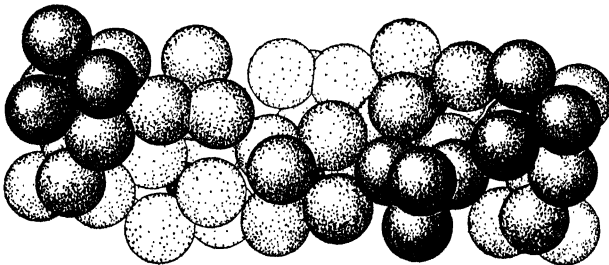


FIG. 319b.—A packing drawing of a . The Ni atoms appear as black spheres within their H_2O octahedra; S atoms do not show.

The structure as a whole is a packing of SO_4 tetrahedra and $(Ni \cdot 6H_2O)$ octahedra (Figure 319).

(*bf*) In a recent study a set of atomic positions, developed from C_{31}^1 , has been proposed for $SrCl_2 \cdot 6H_2O$. They are:

Sr: (a) 000 Cl: (d) $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3}\frac{1}{3}\bar{u}$ with $u=\frac{1}{2}$
 H_2O : (g) $\pm(xyz)$; $\pm(y-x, \bar{x}, z)$; $\pm(\bar{y}, x-y, z)$ with $x=y=0.387$, $z=0.0$.

The published data, which are scanty, are insufficient to establish this structure.

(bg) The previously chosen unit for $MgPt(CN)_4 \cdot 7H_2O$ ($a_0=14.6$ A, $c_0=3.13$ A) was too small. The true cell is twice as high, $c_0=6.26$ A, and contains four molecules.

(bh) The space group of the four-molecule cell of $3CdSO_4 \cdot 8H_2O$ is said to be C_{2h}^6 .

(bi) Estimates of the intensities of powder lines have been used to suggest the following atomic arrangement, based on D_{4h}^1 , for $SrO_2 \cdot 8H_2O$:

Sr: (a) 000 O: (h) $\frac{1}{2}\frac{1}{2}w$; $\frac{1}{2}\frac{1}{2}\bar{w}$ with $w=0.10$
 H_2O : (r) $\pm(uuv)$; $\pm(u\bar{u}v)$; $\pm(\bar{u}\bar{u}v)$; $\pm(\bar{u}uv)$ with $u=0.20$, $v=0.25$.

In this arrangement strontium atoms are surrounded by cubes of H_2O molecules with the somewhat short Sr- H_2O distance of 2.26 A; inside the O_2 group the atomic separation is 1.11 A.

(bj) The large unit found for $2Na_3PO_4 \cdot NaF \cdot 19H_2O$ holds 40 molecules. The data are those demanded by O_h^8 .

(bk) The unit cubes of several **phosphotungstic** and **phosphomolybdic acids** and their salts crystallizing with 30 ± 1 molecules of H_2O have been found to contain eight molecules. Their space group is said to be O_h^4 .

Powder photographic data have been used to determine the shape and size of the $PW_{12}O_{40}$ anion in the partially dehydrated $H_3PW_{12}O_{40} \cdot 5$, or 7, H_2O and to suggest probable positions for the H_2O molecules. The unit cube of this lower hydrate contains two molecules; the atoms of its anions are in the following special positions of O_h^4 :

P: (2a) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
W: (24u) uuv ; $u\bar{u}\bar{v}$; $\bar{u}u\bar{v}$; $\bar{u}\bar{u}v$; vuu ; $\bar{v}u\bar{u}$; $\bar{v}\bar{u}u$; $v\bar{u}\bar{u}$; uvu ; $\bar{u}\bar{v}u$; $u\bar{v}\bar{u}$; $\bar{u}v\bar{u}$;
 $\frac{1}{2}-u$, $\frac{1}{2}-u$, $\frac{1}{2}-v$; $\frac{1}{2}-u$, $u+\frac{1}{2}$, $v+\frac{1}{2}$; $u+\frac{1}{2}$, $\frac{1}{2}-u$, $v+\frac{1}{2}$;
 $u+\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}-v$; $\frac{1}{2}-v$, $\frac{1}{2}-v$, $\frac{1}{2}-u$; $v+\frac{1}{2}$, $\frac{1}{2}-u$, $u+\frac{1}{2}$;
 $v+\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}-u$; $\frac{1}{2}-v$, $u+\frac{1}{2}$, $u+\frac{1}{2}$; $\frac{1}{2}-u$, $\frac{1}{2}-v$, $\frac{1}{2}-u$;
 $u+\frac{1}{2}$, $v+\frac{1}{2}$, $\frac{1}{2}-u$; $\frac{1}{2}-u$, $v+\frac{1}{2}$, $u+\frac{1}{2}$; $u+\frac{1}{2}$, $\frac{1}{2}-v$, $u+\frac{1}{2}$

with $u=0.205$, $v=0.006$

O(1): (8d) $u'u'u'$; $\bar{u}'u'\bar{u}'$; $\frac{1}{2}-u'$, $\frac{1}{2}-u'$, $\frac{1}{2}-u'$; $u'+\frac{1}{2}$, $\frac{1}{2}-u'$, $u'+\frac{1}{2}$;
 $u'\bar{u}'\bar{u}'$; $\bar{u}'\bar{u}'u'$; $\frac{1}{2}-u'$, $u'+\frac{1}{2}$, $u'+\frac{1}{2}$; $u'+\frac{1}{2}$, $u'+\frac{1}{2}$, $\frac{1}{2}-u'$

with $u=0.081$

O(2): (24u) $u_1u_1v_1$; etc. with $u_1=-0.080$, $v_1=-0.234$

O(3): (24u) $u_2u_2v_2$; etc. with $u_2=0.123$, $v_2=0.292$

O(4): (24u) $u_3u_3v_3$; etc. with $u_3=-0.312$, $v_3=-0.008$.

The shape of one of these $PW_{12}O_{40}$ ions is shown in Figure 320. It consists of a central PO_4 tetrahedron and 12 surrounding WO_6 octahedra that share oxygen atoms with it. The H_2O molecules are considered to be of two sorts: three in the positions: $(6e) 00\frac{1}{2}; \frac{1}{2}00; 0\frac{1}{2}0; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$ and four at $(4e) \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}$, if the crystal is a heptahydrate.

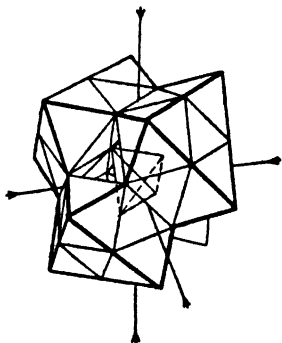


FIG. 320.—The $PW_{12}O_{40}$ ion is considered to have a shape suggested by this diagram. The central P atom is surrounded by four O atoms at the corners of the dotted tetrahedron. About it are 12 oxygen octahedra which share atoms with one another and with the PO_4 group and which have W atoms at their centers (after 1934, 131).

(bl) The unit assigned to the complex phosphate wavellite, $4(PO_4)Al \cdot 2Al(OH)_3 \cdot 9H_2O$, is bimolecular.

(bm) The unit cell of legrandite has one molecule of the composition $Zn_{14}(AsO_4)_9OH \cdot 12H_2O$.

(bn) The monoclinic unit given to $[Co_{(NH_3)_6}^{CO}]_2SO_4 \cdot 3H_2O$ contains two molecules; the space group is thought to be C_6^4 .

(bo) Two molecules are found in the unit of $MgNH_4AsO_4 \cdot 6H_2O$; its space group is C_{2v}^7 .

(bp) The structure recently developed for $LiClO_4 \cdot 3H_2O$ differs from that previously found for the isomorphous $LiI \cdot 3H_2O$ (f) in the positions of the lithium atoms. In the perchlorate, atoms are in the following special positions of C_{6v}^4 :

Li: (a) $00u_1; 0, 0, u_1 + \frac{1}{2}$ with $u_1 = 0.25$

Cl: (b) $\frac{1}{3}\frac{2}{3}u'; \frac{2}{3}, \frac{1}{3}, u' + \frac{1}{2}$ with $u' = 0$

O(1): (b) $\frac{1}{3}\frac{2}{3}w; \frac{2}{3}, \frac{1}{3}, w + \frac{1}{2}$ with $w = 0.278$

O(2): (c) $u\bar{v}; 2\bar{u}, \bar{u}, v; u, 2u, v; \bar{u}, u, v + \frac{1}{2}; 2u, u, v + \frac{1}{2}; \bar{u}, 2\bar{u}, v + \frac{1}{2}$

with $u = 0.439, v = -0.092$

H_2O : (c) $u_2\bar{u}_2v_2$; etc. with $u_2 = 0.125, v_2 = 0.50$.

This arrangement, which coordinates six H_2O molecules about each lithium atom (Figure 321), is practically identical with one found from quantitative spectrometric data.*

* Unpublished measurements of R. B. Corey in this laboratory. The parameters derived from this study are $u_1(Li) = 0.25, u'(Cl) = 0, w(O) = 0.265, u(O) = 0.435, v(O) = -0.09, u_2(H_2O) = 0.125, v_2(H_2O) = 0.50$.

It is probable that the lithium atoms in $\text{LiI} \cdot 3\text{H}_2\text{O}$ should be in (a) $00u_1; 0, 0, u_1 + \frac{1}{2}$ instead of the earlier (b) $\frac{1}{3}\frac{2}{3}u_1; \frac{2}{3}, \frac{1}{3}, u_1 + \frac{1}{2}$. Photographic data lead to the parameters: $u_1(\text{Li})=0.25$, $u'(I)=0$, $u_2(\text{H}_2\text{O})=0.142$, $v_2(\text{H}_2\text{O})=0.50$.

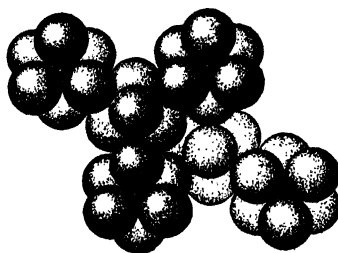
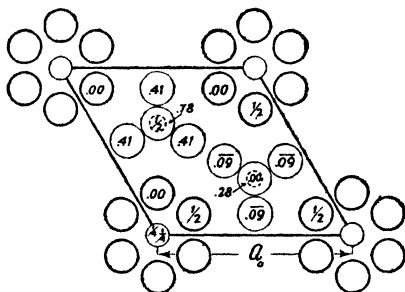


FIG. 321a.—(left) A basal projection of the structure found for $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. Li atoms are at the corners of the diagram surrounded by the heavily outlined water molecules.

FIG. 321b.—(right) A packing drawing of a showing the tetrahedral ClO_4 ions and (black) Li ions equidistant from six H_2O molecules. The O atoms and H_2O molecules, of equal size, are not distinguished by different shadings.

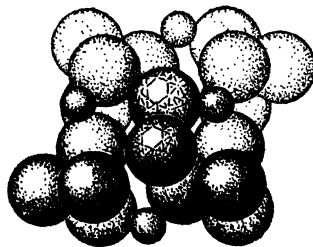
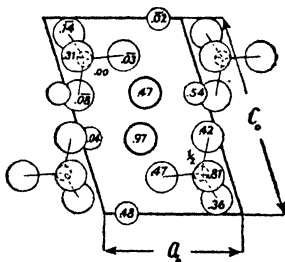


FIG. 321c.—(left) A projection upon its b-face of the monoclinic structure deduced for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Atoms of the SO_4 ions are connected by light lines; the H_2O molecules are heavily ringed.

FIG. 321d.—(right) A packing drawing of c with the H_2O molecules distinguished by line-shading. The S atoms within their tetrahedra cannot be seen.

(bq) The hexagonal unit prism of $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ is bimolecular. The space group is reported to be C_6^2 or C_{6h}^2 .

(br) The atoms of the two $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ molecules contained within the unit cell are in general positions of C_2^2 with the coordinates (a) xyz ; \bar{x} , $y + \frac{1}{2}$, \bar{z} . Parameters, determined from photographic data, are those of Table VII. In this structure (Figure 321c and d) the lithium atoms are

TABLE VII. PARAMETERS OF THE ATOMS IN $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

Atom	x	y	z
S	0.208	0.000	-0.211
O(1)	.153	-.139	-.083
O(2)	.500	-.014	-.192
O(3)	.078	-.078	-.397
O(4)	.161	.305	-.197
H_2O	.569	.472	-.386
Li(1)	-.069	.542	-.386
Li(2)	.167	.478	.003

surrounded by tetrahedra consisting of three sulfate oxygen atoms and one H_2O molecule.

(bs) The unit prism of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ contains four molecules; its space group is said to be V_h^{16} .

(bt) Four molecules are within the cell of $\text{AgNO}_3 \cdot 2\text{NH}_3$. The space group is C_{2v}^{10} .

Miscellaneous Inorganic Compounds

(ca) The cube lengths found for a large number of atopites and atopite-like minerals, and for ochers of calcium and of lead vary between ca 10.25 Å and ca 10.43 Å.

(cb) A partial atomic arrangement for azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, has been based on some rotation photographs and spectrometer data. Copper atoms have been placed in (a) 000; $0\frac{1}{2}\frac{1}{2}$ and in general positions of C_{2h}^5 : (e) $\pm(xyz)$; $\pm(\bar{x}, y + \frac{1}{2}, \frac{1}{2} - z)$ with $x=0.25$, $y=0.486$, $z=0.083$. Suggested parameters for the other atoms are not proved by the existing data.

(cc) The mineral hambergite, $\text{Be}_2\text{BO}_3(\text{OH})$, has been given a structure which explains both a series of spectrometric intensities and the qualita-

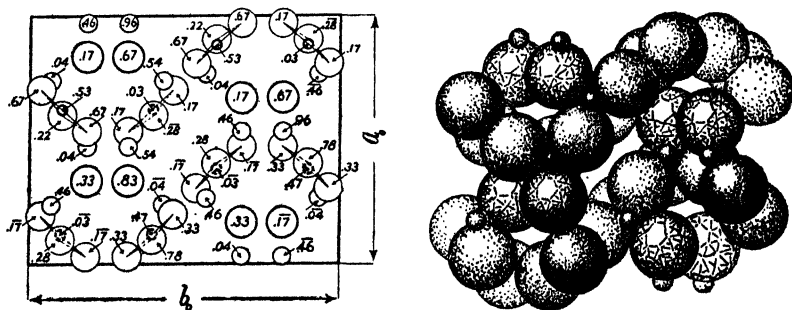


FIG. 322a.—(left) A projection upon the c -face of the orthorhombic structure assigned to hambergite, $\text{Be}_2\text{BO}_3(\text{OH})$. Atoms of the BO_3 groups are connected by light lines. Intermediate circles represent Be atoms; the (OH) groups are heavily ringed.

FIG. 322b.—(right) A packing drawing of a . Small spheres are the Be atoms; the Be atoms do not show. Hydroxyl groups are line-shaded.

TABLE VIII. THE CRYSTAL STRUCTURES OF MISCELLANEOUS INORGANIC COMPOUNDS

Substance, symmetry and type	a_0	b_0	c_0	Space group	No. mol. per cell	References
Arsenoklasite						
$Mn_3(AsO_4)_2 \cdot 2Mn(OH)_2$	9.19	18.01	5.79		4	1931, 10.
$AsI_3 \cdot 3S_8$	14.2		4.48	C_{2v}^6	1	1931, 186.
Atopites (Ca, Mn, Na) $_2$ Sb $_2$ (O, OH, F) $_7$	(ca)					1932, 323, 324; 1933, 4.
Azurite	(cb)					
$2CuCO_3 \cdot Cu(OH)_2$	4.96	5.83	10.27	C_2^6	2	1932, 72; 1933, 71.
Bindheimite	(ca)		$\beta = 87^\circ 36'$		8	1933, 316.
$Pb_2Sb_2O_7$	10.44					
Binnite	(ct)				2	1934, 205.
(Cu, Fe) $_{12}$ As $_3$ S $_{13}$	10.19			T_d^2		
Boleite						1930, 105b.
Boracite	(ax), (ct)				8	1932, 307; 1933, 201; 1934, 171.
$Mg_2ClB_7O_{13}$ (low temp. form)	17.07	17.07	12.07			
Boracite	(ct)				4	1932, 307; 1934, 171.
$Mg_3ClB_7O_{13}$ (high temp. form, $> 265^\circ C$)	12.1					
Bourmonite					4	1932, 307; 1934, 171.
$CuPb_3S_8$	8.10	8.65	7.75	V_b^{11}	4	1932, 343.
$CHL_4 \cdot 3S_8$	14.1		4.44	C_{2v}^6	1	1931, 186.
Cumengeite					8	1930, 105b.
Hamburgite	(cc)				8	1931, 495.
$Be_2BO_3(OH)$	9.73	12.18	4.42	V_b^{15}		
Hanksite	10.52		21.25	C_6^h	2	1931, 134.
$9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$						
Koppite	(ca)				8	1931, 57.
(Ca, Ce, Na, K) $_2$ (Cb, Fe) $_2$ O $_6$ (O, OH, F)	10.37					
Lewisite	(ca)				8	1932, 298.
(Ca, Fe, Na) $_2$ (Sb, Tl) $_2$ (O, OH) $_7$	10.269					
Malachite	(cd)				4	1932, 71; 1933, 71.
$CuCO_3 \cdot Cu(OH)_2$	9.38	11.95	3.18	C_2^h		
		$\beta = 91^\circ 03'$				

<i>Substance, symmetry and type</i>	a_0	b_0	c_0	<i>Space group</i>	<i>No. mol. per cell</i>	<i>References</i>
Microelite (Ca, Na) ₂ (Ta, Cb) ₂ (O, F) ₇	10.381				8	1933, 374.
Northupite Na ₂ Mg(CO ₃) ₂ ·NaCl	13.98			T _h ¹	16	1931, 134, 413; 1933, 491.
Brominated Northupite Na ₄ Mg(CO ₃) ₂ ·NaBr	14.17			T _h ¹	16	1931, 413.
Triphosphonitrite (PNCI ₂) ₃	14.00	6.16	12.94	V _h ¹⁶	4	1932, 235.
Tetraphosphonitrite (PNCI ₂) ₄	10.79		5.98	C _{4h}	2	1932, 235.
Potassium Trithionate K ₃ S ₃ O ₆	9.77	13.63	5.76	V _h ¹⁶	4	1934, 305, 305b.
Potassium Pyrosulfite K ₂ S ₂ O ₅	6.95	6.19	7.55	C _{2h}	2	1932, 487, 490.
Pseudoboleite						1930, 105b.
Pyrrhite	10.40				8	1932, 296.
Pyrosaurite Fe(OH) ₂ ·3Mg(OH) ₂ ·3H ₂ O	3.089		23.23		4	1931, 11.
Pyrochlore (Na, Ca) ₂ (Cb, Tl) ₂ (O, F) ₇	10.376				8	1930, 391.
Romeite (Ca, Na, Mn) ₂ Sb ₂ (O, OH, F) ₇	10.261				8	1932, 324, 496; 1933, 316.
Schneebergite (Ca, Na, Fe) ₂ Sb ₂ O ₆ (OH)	10.296				8	1932, 496.
Sulphohalite 2Na ₂ SO ₄ ·NaCl·NaF	10.08			O _h ²	4	1934, 347.
Tetradymite	10.31		$\alpha=24^\circ 10'$		1	1934, 332.
Tychite 2MgCO ₃ ·2Na ₂ CO ₃ ·Na ₂ SO ₄	13.90			T _h ¹	8	1931, 413; 1933, 491.
Voltaïtes						1932, 171; 1933, 150, 151.
Basic Zinc Chloride ZnCl ₂ ·4Zn(OH) ₂	12.56		15.84		8	1933, 131.

tive data from oscillation photographs. Atoms in its eight-molecule unit are in general positions (c) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, \bar{z})$; $\pm(\bar{x}, y+\frac{1}{2}, \frac{1}{2}-z)$; $\pm(\frac{1}{2}-x, \bar{y}, z+\frac{1}{2})$ of V_h^{15} with the coordinates listed in Table IX. The axes of this description are the same as those of 1930, 352, p. 64.

As can be seen from Figure 322a and b the grouping consists of linked BO_3 triangles and $Be(O_3OH)$ tetrahedra. Each oxygen atom is shared by one B and two Be atoms; OH groups join two Be atoms.

TABLE IX. PARAMETERS OF THE ATOMS IN HAMBERGITE

Atom	No. per cell	x	y	z
Be(1)	8	-0.031	0.183	0.458
Be(2)	8	.236	.069	.458
B	8	.117	.103	-.028
O(1)	8	.031	.183	-.167
O(2)	8	.097	.103	.278
O(3)	8	.194	.037	-.167
OH	8	-.167	.183	.167

(cd) The copper atoms of the four molecules of $CuCO_3 \cdot Cu(OH)_2$ lying in the unit cell of malachite are reported to be in two sets of general positions of C_{2h}^6 : (e) $\pm(xyz)$; $\pm(\frac{1}{2}-x, y+\frac{1}{2}, \bar{z})$ with the parameters $x=0$, $y=0.208$, $z=0.125$, $x'=0.264$, $y'=0.104$, $z'=0.625$. The other atomic parameters have not been found.

(ce) Some photographic data have been used in assigning a structure to northupite, $Na_2Mg(CO_3)_2 \cdot NaCl$. According to this arrangement the 16 molecules of its unit cube are in the following special and general positions of T_h^4 (1930, 352, p. 125):

Mg: (16c) $\frac{5}{8}\frac{5}{8}\frac{5}{8}$; $\frac{5}{8}\frac{7}{8}\frac{7}{8}$; $\frac{7}{8}\frac{5}{8}\frac{7}{8}$; $\frac{7}{8}\frac{7}{8}\frac{5}{8}$ and 3 sets of similar points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$

Cl: (16b) $\frac{1}{8}\frac{1}{8}\frac{1}{8}$; $\frac{1}{8}\frac{3}{8}\frac{3}{8}$; $\frac{3}{8}\frac{1}{8}\frac{1}{8}$; $\frac{3}{8}\frac{3}{8}\frac{1}{8}$ and 3 sets of similar points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$

C: (32b) uuu ; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$; $\frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u$; $\frac{1}{4}-u, u+\frac{1}{4}, u+\frac{1}{4}$; $u+\frac{1}{4}, \frac{1}{4}-u, u+\frac{1}{4}$; $u+\frac{1}{4}, u+\frac{1}{4}, \frac{1}{4}-u$ and similar points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$ with $u(C)=0.405$

Na: (48c) $u00$; $\bar{u}00$; $0u0$; $0\bar{u}0$; $00u$; $00\bar{u}$;
 $\frac{1}{4}-u, \frac{1}{4}, \frac{1}{4}$; $u+\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}-u, \frac{1}{4}$; $\frac{1}{4}, u+\frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}-u$; $\frac{1}{4}, \frac{1}{4}, u+\frac{1}{4}$
 and similar points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$ with $u(Na)=0.225$

O: (g) xyz ; $x\bar{y}\bar{z}$; $\bar{x}y\bar{z}$; $\bar{x}\bar{y}z$; zxy ; $\bar{z}x\bar{y}$; $\bar{z}\bar{x}y$; $z\bar{x}\bar{y}$; yzx ; $\bar{y}\bar{z}x$; $y\bar{z}\bar{x}$; $\bar{y}z\bar{x}$;
 $\frac{1}{4}-x, \frac{1}{4}-y, \frac{1}{4}-z$; $\frac{1}{4}-x, y+\frac{1}{4}, z+\frac{1}{4}$; $x+\frac{1}{4}, \frac{1}{4}-y, z+\frac{1}{4}$;
 $x+\frac{1}{4}, y+\frac{1}{4}, \frac{1}{4}-z$; $\frac{1}{4}-z, \frac{1}{4}-x, \frac{1}{4}-y$; $z+\frac{1}{4}, \frac{1}{4}-x, y+\frac{1}{4}$;
 $z+\frac{1}{4}, x+\frac{1}{4}, \frac{1}{4}-y$; $\frac{1}{4}-z, x+\frac{1}{4}, y+\frac{1}{4}$; $\frac{1}{4}-y, \frac{1}{4}-z, \frac{1}{4}-x$;
 $y+\frac{1}{4}, z+\frac{1}{4}, \frac{1}{4}-x$; $\frac{1}{4}-y, z+\frac{1}{4}, x+\frac{1}{4}$; $y+\frac{1}{4}, \frac{1}{4}-z, x+\frac{1}{4}$ and similar
 points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$. The chosen parameters are $x=0.392$, $y=0.348$, $z=0.475$.

The arrangement given to tychite, $\text{Na}_4\text{Mg}_2(\text{CO}_3)_4 \cdot \text{Na}_2\text{SO}_4$, is like this northupite grouping with Na_2SO_4 in place of 2NaCl . The eight sulfur atoms in the unit cube are at $(8f) 000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}$. Sulfate oxygen atoms are in $(32b) u'u'u'$; etc. with $u'(O)=0.062$. The other atoms are placed as in northupite: Mg in $(16c)$; C in $(32b)$ with $u=0.400$; Na in $(48c)$ with $u=0.225$ and carbonate oxygens in (g) of T_h^4 with $x=0.375, y=0.352, z=0.473$.

(cf) From spectral photographic data it has been found that the atoms in potassium trithionate, $\text{K}_2\text{S}_3\text{O}_6$, are in the following positions of V_h^{10} :

$$(c) \pm(uv\frac{1}{4}); \pm(\frac{1}{2}-u, v+\frac{1}{2}, \frac{3}{4}) \quad (d) \pm(xyz); \pm(x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z); \\ \pm(x, y, \frac{1}{2}-z); \pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$$

with the parameters of Table X. In this structure (Figure 322c) S-O within the same ion is ca 1.50 Å, S-S=2.19 Å and the angle joining the three sulfur atoms is 103° .

TABLE X. PARAMETERS OF THE ATOMS IN $\text{K}_2\text{S}_3\text{O}_6$

Atom	No. per cell	Position	x	y	z
K(1)	4	(c)	0.131	0.089	0.25
K(2)	4	(c)	.180	-.236	.25
S(1)	4	(c)	.033	.319	.25
S(2)	4	(c)	.083	.472	.25
S(3)	4	(c)	.305	.472	.25
O(1)	4	(c)	-.125	.305	.25
O(2)	4	(c)	.347	.583	.25
O(3)	8	(d)	.083	.278	.042
O(4)	8	(d)	.361	.417	.042

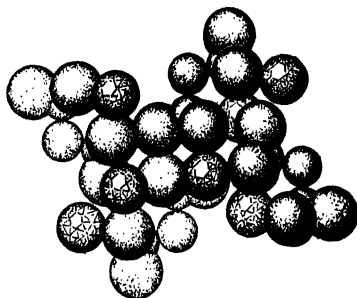
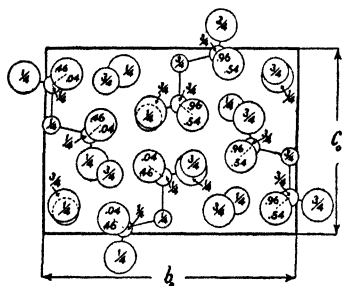


FIG. 322c.—(left) The structure found for $\text{K}_2\text{S}_3\text{O}_6$ projected on the a-face of its orthorhombic cell. Largest circles are O atoms, intermediate circles K ions. Atoms of the S_3O_6 ions are connected by light lines.

FIG. 322d.—(right) A packing drawing of c. The K ions are line-shaded. No significance is to be attached to the radii chosen for sulfur.

(cg) Estimated intensities on oscillation photographs have been used in choosing a structure for **potassium pyrosulfite**, $K_2S_2O_5$. The atoms in its two-molecule cell are placed in the following special and general positions of C_{2h}^2 : (e) $\pm(u\frac{1}{2}v)$, (f) $\pm(xyz)$; $\pm(x, \frac{1}{2}-y, z)$ with the parameters of Table XI. The pyrosulfite ion resulting from this arrangement has the structure O_3S-SO_2 (Figure 323) with a S-S distance of 2.18 Å.

(ch) It is natural to infer from the fractional number of molecules found in the unit of **pyroaurite** that either the formula, the cell size or

TABLE XI. PARAMETERS OF THE ATOMS IN $K_2S_2O_5$

Atom	No. per cell	Position	x	y	z
K(1)	2	(e)	0.22	0.25	0.95
K(2)	2	(e)	.65	.25	.67
S(1)	2	(e)	.70	.25	.22
S(2)	2	(e)	.01	.25	.32
O(1)	4	(f)	.07	.06	.24
O(2)	4	(f)	.63	.06	.31
O(3)	2	(e)	.67	.25	.03

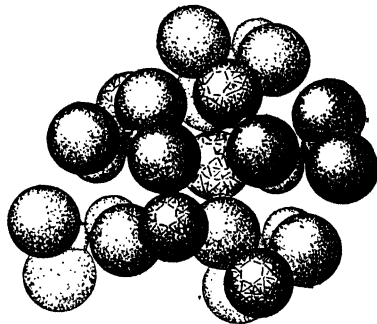
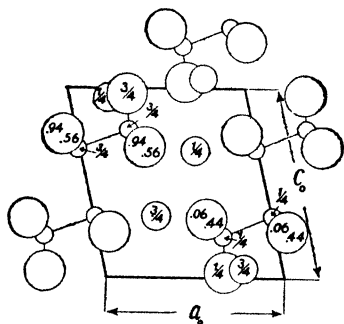


FIG. 323a.—(left) The monoclinic structure of $K_2S_2O_5$ projected on its b -face. Oxygen atoms are represented by the largest, S by the smallest circles. The light lines joining them outline the S_2O_5 ions.

FIG. 323b.—(right) A packing drawing of a . The size given the S atoms was determined by convenience only. K ions are line-shaded.

the density is in error. Existing data contain no evidence for a larger cell and the formula is said to be substantially correct.

(ci) A large number of the cubic or pseudo-cubic **voltaites** have been prepared and their unit cells measured (see Table XII). The composition of these sulfates is still uncertain though a recent study (1932, 171) places it as approximately $(SO_4)_{12}Fe_4^{++}R_5^{++}R_2^+ \cdot 16-18H_2O$.

(cj) A structure has been found for the complex sulfide **binnite**, $(Cu, Fe)_{12}As_4S_{13}$, which, except for the addition of two extra sulfur atoms and

TABLE XII. UNIT CUBE SIZE OF VOLTAITES

Voltaite	a_0	Voltaite	a_0
K-Cd compound	27.54	Rb-Cd compound	27.80
K-Fe ⁺⁺	27.33	Rb-Fe ⁺⁺	27.60
K-Mn ⁺⁺	27.25	Rb-Mn ⁺⁺	27.60
K-Zn	27.10	Rb-Zn	27.15
NH ₄ -Cd	27.85	Tl-Cd	27.69
NH ₄ -Fe ⁺⁺	27.35	Tl-Fe ⁺⁺	27.43
NH ₄ -Mg	27.42	Tl-Mn ⁺⁺	27.71
NH ₄ -Mn ⁺⁺	27.55	Tl-Zn	27.01

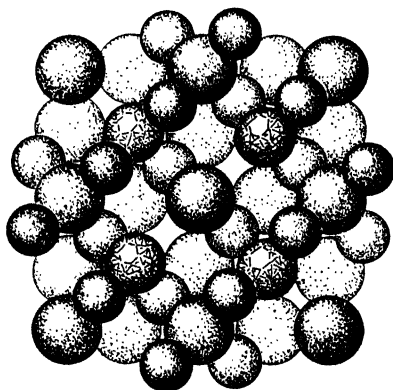
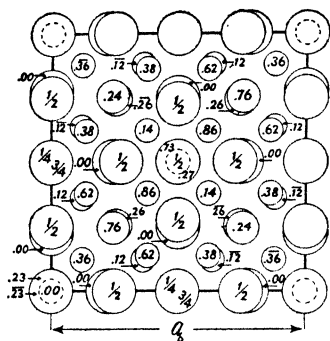


FIG. 324a.—(left) A cube face projection of the structure of binnite, $(\text{Cu, Fe})_{12}\text{As}_4\text{S}_{18}$. The largest circles are (Cu, Fe) , the smallest are S atoms.

FIG. 324b.—(right) A packing drawing showing the bottom half of the unit cube of binnite. The atoms have their neutral radii; As atoms are line-shaded.

somewhat altered parameters, is identical with that previously determined for tetrahedrite, $(\text{Cu, Ag})_3(\text{Sb, As})\text{S}_3$ [XV, (p), p. 280]. The binnite arrangement, as developed from photographic data, places the atoms of its two-molecule cube in positions (of T_d^3):

Cu, Fe(1): (12a) $u00$; etc. with $u=0.225$

Cu, Fe(2): (12h) $\frac{1}{2}0\frac{1}{4}$; etc.

As: (8a) $u'u'u'$; etc. with $u'=0.255$

S(1): (24g) vwv ; etc. with $v=0.122$, $w=0.363$

S(2): (2a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

The packing is that to be expected from neutral atoms. It is instructive to compare the atomic environments in this arrangement (Figure 324a and b) with those prevailing in enargite, Cu_3AsS_4 [XVIA, (an)]. All the sulfurs in enargite and those [in (24g)] which are common to both binnite

and tetrahedrite have four metal atoms tetrahedrally placed about them. The two binnite sulfurs at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ are enclosed by six octahedrally grouped (Cu, Fe) atoms. In enargite the copper and arsenic atoms are tetrahedrally surrounded but in binnite and tetrahedrite the metal environments are more complex. Arsenic atoms and the Cu, Fe(1) atoms in (12a) have only three neighboring sulfurs; four sulfurs, however, are to be found about Cu, Fe(2) in (12h).

(ck) The mineral **boracite**, with eight molecules of the composition $Mg_6Cl_2B_{14}O_{26}$ in its orthorhombic unit, has recently been assigned one of the space groups C_{2v}^{12} or C_{2v}^{14} . Previous studies had preferred C_{2v}^{11} .

Above 265° C this mineral is cubic with a four-molecule cell. Possible space groups and structures have been discussed but no definite conclusions have been reached.

(cl) It has been shown that the photographically observed powder lines of **sulphohalite**, $2Na_2SO_4 \cdot NaCl \cdot NaF$, can be explained in terms of the following arrangement based on O_h^5 (Figure 324c):

- F: (4b) $000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$ Cl: (4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00$
 S: (8e) $\pm(\frac{1}{4}\frac{1}{4}\frac{1}{4}); \pm(\frac{1}{4}\frac{3}{4}\frac{3}{4}); \pm(\frac{3}{4}\frac{1}{4}\frac{3}{4}); \pm(\frac{3}{4}\frac{3}{4}\frac{1}{4})$
 Na: (24a) $u'00$; etc. (see book, p. 303) with $u'=0.226$
 O: (32a) $\pm(uuu); \pm(u\bar{u}\bar{u}); \pm(\bar{u}\bar{u}u); \pm(\bar{u}u\bar{u})$ and 3 sets of similar points about $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$ (1930, 352, p. 110) with $u=0.164$.

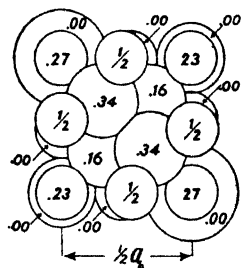


Fig. 324c.—A cube face projection of one eighth of the unit of sulphohalite, $2Na_2SO_4 \cdot NaCl \cdot NaF$. The circles have the radii of their corresponding atoms; in order of decreasing size they refer to Cl^- , O, F^- and Na^+ .

(cm) The sulfide mineral **tetradymite**, Bi_2Te_2S , has an elongated rhombohedral unit containing one molecule. From photographic data it has been found that atoms are in the following positions:

- S: 000 Bi: $\pm(uuu)$ with $u=0.392$ Te: $\pm(vvv)$ with $v=0.788$.

This yields a structure which is a succession of layers of atoms of a kind normal to the three-fold axis. The shortest interatomic distances are: Bi-S=3.05 Å, Bi-Te=3.12 Å, Te-Te=3.69 Å.

Chapter XIXA. Structures of the Silicates

Some of the work of the last three years has been devoted to simple silicates not yet analyzed, some to a revision of previous studies, but for the most part it has been concerned with more complex mineral types whose structures are still imperfectly understood. Most of these are either sheet structures, like the micas, or network groupings, such as the sodalite minerals and the zeolites. The zeolites are of especial interest because of the way they can be dehydrated and can reabsorb water without destruction of their atomic frameworks; approximate arrangements have been deduced for several which aid in understanding how this can occur. Real progress is also being made towards unraveling the crystal structures of the feldspars, one of the few important groups of the silicate minerals for which reasonable atomic arrangements have not been proposed.

A, I. Simple Orthosilicates

(*ak*) A reinvestigation of the structure of **andalusite**, Al_2SiO_5 , has led to slightly changed parameters in the X direction for the atoms O(3), O(4) and Al(2) (see Table IX, book, p. 333). The new arrangement, with $x(\text{O}, 3)=0.11$, $x(\text{O}, 4)=0.25$, $x(\text{Al}, 2)=-0.125$, agrees with the earlier one in giving aluminum atoms an oxygen coordination of five.

(*al*) A considerably altered grouping has been proposed for **sillimanite**, Al_2SiO_5 . This structure yielding good agreement with the lines observed on a powder photograph differs from the previous one in having regular SiO_4 tetrahedra. Atoms are in the same special positions of V_h^{1b} as before (book, pp. 331 and 293) with the new parameters listed in Table II.

(*am*) A structure has been assigned to the **high** temperature cubic form of **carnegieite**, NaAlSiO_4 , which, if its silicate and aluminate tetrahedra are considered equivalent, is closely related to that of high cristobalite. This arrangement gives calculated intensities agreeing with a powder photograph made at ca 760°C . The atoms in its four-molecule cube are in the following positions of T^4 (book, p. 267):

TABLE I. THE CRYSTAL STRUCTURES OF THE SILICATES

Substance, symmetry and type		a_0	b_0	c_0	Space group	No. mol. per cell	References
Acmite $\text{NaFe}(\text{SiO}_3)_2$	Mon. (at)	9.71	8.89	5.24	C_{2h}^6	2	1931, 464.
Afwillite $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$	Mon. (bm)	11.39	5.47	13.09	C_2^2	4	1932, 172.
Albite $\text{NaAlSi}_3\text{O}_8$	Tri. (tl), (u)	8.14	12.86	7.17	C_1^1	4	1934, 262.
Amphibole (var. Pargasite)	Mon. (w), (bb)	$\alpha=94^\circ 3'$, $\beta=116^\circ 29'$, $\gamma=88^\circ 9'$	17.70	10.92			1931, 139.
Analcite $\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$	Pseudo-cub. (g), (ak)	9.88	$\beta=98^\circ 26'$				1931, 158, 242.
Andalusite Al_2SiO_5	Ort. (ah), (ba)	13.684	$\beta=\text{ca } 102^\circ$				1931, 204.
Apophyllite $\text{KF} \cdot \text{Ca}_2\text{Si}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$	Tet. Ort.	9.00		15.8	D_{2h}^4	2	1931, 443.
Ardennite $(\text{SiO}_3)_2\text{AsO}_4\text{Al}_2\text{Mn}(\text{AlOH})_2\text{Mn}_4 \cdot 2\text{H}_2\text{O} (?)$	Ort. Tet.	18.56	5.83	8.72	V_h^{12}	2	1932, 175.
Ashcroftine $\text{NaK}(\text{Ca}, \text{Mg}, \text{Mn})\text{AlSi}_5\text{O}_{18} \cdot 8\text{H}_2\text{O}$	Ort.	34.04		17.49		40	1933, 195.
Astrophyllite $[\text{Si}_2\text{O}_7]_2[(\text{Ti}, \text{Zr})(\text{OH}, \text{F})_2](\text{Fe}, \text{Mn})_4(\text{K}, \text{Na})_2$	Ort.	11.70	5.40	21.10		4	1934, 91.
Axinite $\text{MgHCa}_2\text{BA}_k(\text{SiO}_4)_4$	Ort.	12.87	7.15	8.91		2	1932, 172.
Bavenite $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{BeO} \cdot 4\text{CaO} \cdot \text{H}_2\text{O}$	Ort.	9.67	11.53	4.95	$V_h^1 (?)$	1	1933, 276.
Bertrandite $\text{H}_2\text{Be}_2\text{Si}_2\text{O}_7$	Ort. (as)	15.19	8.67	4.53	C_{2v}^{12}	4	1932, 232.

Substance, symmetry and type		a_0	b_0	c_0	Space group	No. mol. per cell	References
Braunite	Tet.	9.50		18.98	D_{2h}^{20}	8	1931, 9.
$3Mn_2O_3 \cdot MnSiO_3$							
Cancrinite	Hex.	12.72		5.18	C_6^1 (?)	1	1930, 457; 1932, 275; 1933, 269, 270.
$3(Na_2Al_2O_4 \cdot 2SiO_2) \cdot 2CaCO_3$							
α -Carnegieite	Cub.	7.37 at ca 760° C			T^4	4	1932, 27.
$NaAlSiO_4$							
Chabazite	Hex.	13.75		14.94	D_{2d}^6	2	1931, 488; 1932, 286; 1933, 514.
$Ca_3Al_2Si_3O_{12} \cdot 6H_2O$							
Chlorites	Mon.						
Cyanite	Tri.						
Al_2SiO_5							
Dickite	Mon.	5.14	8.94	14.42	C_4^1	4	1932, 184.
$Al_2Si_2O_7(OH)_4$			$\beta = 96^\circ 50'$				
Edingtonite	Tet. (?)	9.7		6.6	V_d^3	2	1930, 423; 1934, 161. 1931, 204.
$Ba_2Al_4Si_6O_{20} \cdot 8H_2O$							
Enstatite	Ort.	18.16	8.84	5.19	V_h^{15}	16	1932, 436.
(var. Bronzite)							
Epididymite	Ort.	12.63	7.32	13.58	V_h^{16}	8	1934, 119.
$Na_8BeSi_7(OH)$							
Epidote	Mon.	16.39	5.63	10.20		4	1930, 111d; 1931, 74; 1932, 172.
$(SiO_4)_2Al_2Ca_2(Al,Fe)OH$			$\beta = 98^\circ 57'$				
Euclase	Mon.	4.62	14.24	4.75	C_{2h}^6	4	1933, 46.
$HBe_3AlSi_5O_{16}$			$\beta = 79^\circ 44'$				
Eudialyte	Hex.						1930, 105a, 193b.
Eulytite	Cub.	10.272			T_d^6	4	1928, 253a; 1931, 299.
$Bi_4Si_4O_{13}$							
Feldspars	Mon. and Tri.						1929, 289a, 381; 1931, 391; 1933, 467; 1934, 262.

Fuller's Earth $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$	Hex.	10.20	10.00	4	1932, 486.
Garnet	Cub.	(c), (bs)			1933, 182, 521, 522.
Gehlenite (synthetic)	Tet.	(n)	5.10	V_4^2	1930, 437, 438.
Hauynite $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}(1-2, \text{SO}_4)$	Cub.	(aa), (bj)	9.11		1932, 23, 26; 1933, 30; 1934, 162.
Hemimorphite	Ort.	(ag), (ar)	5.11	C_{2v}^{20}	1932, 231.
$\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$	Mon.	(aj), (bt)	15.913	C_{2h}^2	1932, 503; 1933, 514.
Heulandite	Mon.	(l)	17.85		1931, 139, 227; 1934, 128.
Hornblendes*	Mon.	(t)	5.443		1932, 351.
Joaquinite $\text{NaBa}(\text{Ti, Fe})_2\text{Si}_4\text{O}_{18}$	Ort.	9.61	22.4	4	1931, 28.
Kaiofiphilite KAlSiO_4	Hex.	(aj)	8.51	54	1932, 183.
Kaolin $\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4$	Mon.	(az)	14.51	4	1931, 135a.
Lawsonite $\text{Ca}(\text{SiO}_3)_2 \cdot (\text{AlO}_2\text{H}_2)_2$	Ort.	5.14	8.90	C_4^2	1931, 493.
Leucophanite $(\text{Ca, Na})_2\text{BeSi}_2(\text{O, OH, F})_7$	Ort.	5.87	13.22	V_h^{17}	1932, 172.
Lieavrite $\text{CaFe}_2^{++}(\text{Fe}^{+++}\text{OH})(\text{SiO}_4)_2$	Ort.	7.38	9.96	4	
	Ort.	8.82	5.86	4	

*A Korean hornblende of the composition $(\text{O, OH, F})_2(\text{Ca, Na, K})_{2.8}(\text{Mg, Fe, }^{++}\text{Mn, Fe, }^{+++}\text{Ti})_4[(\text{Si, Al})_6\text{O}_{18}]_2$ has $a_0 = 9.77 \text{ \AA}$, $b_0 = 17.85 \text{ \AA}$, $c_0 = 5.32 \text{ \AA}$, $\beta = 73^\circ 58'$.

Substance, symmetry and type		a_0	b_0	c_0	Space group	No. mol. per cell	References
Lusakite	Ort.	7.86	16.62	5.65	V_h^1	1	1934, 246.
$H_2O \cdot 4(Fe, Co, Ni, Mg)O \cdot 9(Al, Fe)_2O_3 \cdot 8H_2O$							
Meliphanite	Tet.	10.58		9.88		8	1931, 493.
Mesolite	Mon.	56.7	6.54	18.44	C_2^1	8	1933, 194, 469.
$Na_2C_2Al_3Si_8O_{30} \cdot 8H_2O$			$\beta = 90^\circ$				
Milarite	Hex.	10.46		13.90	D_{6h}^2	2	1930, 111b.
$HKC_2Al_2(Si_3O_8)_6$							
Montmorillonite	Ort.	5.095	8.83	15.2			1933, 205.
$H_2O \cdot Al_2O_3 \cdot 4SiO_2$							
Muscovite	Mon.	5.18	9.02	20.04	C_2^1	4	1930, 153.
$KAl_2(AlSi_3)O_{10}(OH)_2$			$\beta = 95^\circ 30'$				
Nacrite	Mon.	5.16	8.93	28.66	C_4^1	8	1933, 160.
$Al_3Si_2O_7(OH)_4$			$\beta = 91^\circ 43'$				
Narsarsukite	Tet.	10.78		7.99	C_4^1	4	1932, 174.
$(Si_4O_{11})(Ti, FeF)Na_2$							
Natrolite	Ort.						1931, 489; 1932, 189, 217; 1933, 469, 514.
$Na_2Al_2Si_3O_{10} \cdot 2H_2O$							1931, 28.
Nephelite	Hex.						
$NaAlSi_3O_8$		9.03				1	1932, 23, 26; 1934, 162.
Noeselite	Cub.						
$Na_2Al_6Si_6O_{24} \cdot SO_4$							
Pectolite	Tri.	7.91	7.08	7.05		2	1931, 464.
$NaHC_2(SiO_2)_4$		$\alpha = 90^\circ$, $\beta = 95^\circ 10'$, $\gamma = 103^\circ 0'$					
Pollucite	Cub.	13.66				16	1932, 173.
$(CaAl_2H_4)Si_4O_8$							
Prehnite	Ort.	4.65	5.52	18.53	V_h^1 or C_{2v}^1	2	1931, 135a.
$Ca_2(SiO_3)_2(AlOH)AlO_3H$							

Pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	Mon.	(<i>ay</i>)	5.14	8.90 $\beta = 99^\circ 55'$	18.55		4	1934, 96, 200.
Pyrosmalite $\text{Si}_4\text{O}_7(\text{Mn,Fe})_3(\text{Mn,Fe})(\text{OH,Cl})_2$	Hex.		13.44		7.20		4	1931, 135.
Rinkite $(\text{SiO}_2)_4[(\text{Ti,Ce})\text{F}]\text{Ca}_2\text{Na}$	Ort.	(<i>br</i>)	18.37	5.63	7.42		4	1933, 153; 1934, 90.
Sanidine KAISi_3O_8	Mon.	(<i>bm</i>)	8.45	12.90 $\beta = 116^\circ 6'$	7.15		4	1934, 262.
Scapolite	Tet.	(<i>z</i>), (<i>bt</i>)						1931, 228; 1932, 402.
Scorlite $\text{CaAl}_2\text{Si}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$	Mon. (?)	(<i>y</i>), (<i>bd</i>)	18.44	18.90 $\beta = \text{ca } 90^\circ$	6.53		4	1930, 258; 1933, 469, 514.
Sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Ort.	(<i>f</i>), (<i>at</i>)	7.43	7.58	5.74		4	1931, 204.
Sodalite $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$	Cub.	(<i>x</i>), (<i>bj</i>)	8.89				2	1932, 26.
Disodium Calcium Orthosilicate, $\text{Na}_2\text{CaSiO}_4$	Cub.	(<i>l</i>), (<i>am</i>)	7.49				4	1932, 28, 29.
Spodumene $\text{LiAl}(\text{SiO}_3)_2$	Mon.	(<i>r</i>), (<i>at</i>)	9.50	8.30 $\beta = 69^\circ 40'$	5.24		4	1931, 464.
Talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Mon.	(<i>ay</i>)	5.26	9.10 $\beta = 100^\circ$	18.81		4	1934, 96.
Thaumasite $\text{CaCO}_3 \cdot \text{CaSO}_4 \cdot \text{CaSiO}_3 \cdot 15\text{H}_2\text{O}$	Hex.		10.90		10.29		2	1933, 6.
Thomsonite $\text{Na}_2\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_{10} \cdot 6\text{H}_2\text{O}$	Ort.	(<i>bh</i>)	13.04	13.06	13.22		4	1931, 489; 1932, 216; 1933, 469, 514.

Substance, symmetry and type	a_0	b_0	c_0	Space group	No. mol. per cell	References
Ultramarines (aa), (bf)	15.63	11.83		D_{4h}^4		1930, 154a.
Vesuvianite (ah), (aq)	10.80	10.26	7.26	C_{2h} or C_2^2	4	1930, 193a; 1931, 465; 1932, 294; 1933, 461.
Wöhlerite $(SiO_4)_2(ZrF,CbO)Ca_2Na$ (bg)	7.88	7.27	7.03		6	1933, 152; 1934, 90.
Wollastonite (s), (bn)	$\alpha=90^\circ$, $\beta=95^\circ 16'$, $\gamma=103^\circ 25'$	5.57	10.08		4	1930, 111d; 1932, 172, 175.
Ca_3SiO_4	16.21	$\beta=109^\circ 3'$				
Zoisite $(SiO_4)_2 \cdot Al_2Ca_2(OH)$	13.820	$\beta=90^\circ$		T_d^2	4	1933, 348.
Zuanyite $Al_3Si_4O_{20}(OH,F)_{13}Cl$ (aj), (bk)						

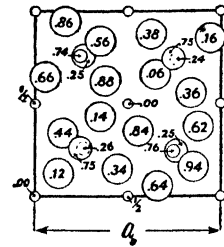


FIG. 325.—A cube face projection of the unit of the structure given to the high temperature (α) modification of carnegieite, $NaAlSiO_4$. In order of decreasing size the circles refer to O, Na, Al and Si atoms.

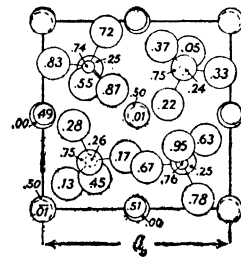


FIG. 326a.—A cube face projection of the atomic arrangement found for Na_2CaSiO_4 . Oxygen atoms are shown as the largest circles, Na by slightly smaller ones. Light lines connecting smallest Si with O atoms outline SiO_4 tetrahedra.

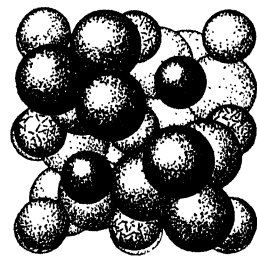


FIG. 326b.—A packing drawing of a. Si atoms cannot be seen; the Ca ions are line-shaded.

TABLE II. PARAMETERS OF THE ATOMS IN SILLIMANITE

Atom	No. per cell	Position	x	y	z
O(1)	4	(c)	0.15	0.07	0.25
O(2)	4	(c)	-.15	-.07	.25
O(3)	4	(c)	.03	.47	.25
O(4)	8	(d)	-.11	.22	0
Si	4	(c)	.14	-.35	.25
Al(1)	4	(a)	0	0	0
Al(2)	4	(c)	-.14	.35	.25

Al: (4f) uuu; etc. with $u=0.258$ Si: (4f) with $u=0$
 Na: (4f) with $u=0.744$ O(1): (4f) with $u=0.125$
 O(2): xyz; etc. with $x=0.658$, $y=0.644$, $z=0.055$.

It will be noticed that this structure (Figure 325) would more closely resemble that of $\text{Na}_2\text{CaSiO}_4$ (*an*) if the Si and Al positions were interchanged; such an alternative grouping would give indistinguishable X-ray effects.

(*an*) A further study of the cubic $\text{Na}_2\text{CaSiO}_4$ has led to a structure that accounts well for powder photographic data and resembles β -cristobalite and α -carnegieite (*am*). It differs from the previously suggested arrangement (book, p. 338) in an interchange of calcium and half the sodium atoms and in the parameters for oxygen lying in general positions. Its atoms (Figure 326) are in the following special positions of T^4 (book, p. 267):

Si: (4f) uuu; with $u=0.258$ Ca: (4f) with $u=-0.007$
 Na(1): (4f) with $u=0.750$ Na(2): (4f) with $u=0.500$
 O(1): (4f) with $u=0.134$ O(2): xyz; etc. with $x=0.555$, $y=0.667$,
 $z=0.222$.

(*ao*) The structure proposed for the cubic mineral **eulytite** yields discrete SiO_4 tetrahedra. Its space group is T_d^6 with bismuth atoms in positions:

(16f) uuu; $u, \bar{u}, \frac{1}{2}-u; \frac{1}{2}-u, u, \bar{u}; \bar{u}, \frac{1}{2}-u, u;$
 $u+\frac{1}{4}, u+\frac{1}{4}, u+\frac{1}{4}; \frac{1}{4}-u, u+\frac{1}{4}, \frac{3}{4}-u; u+\frac{1}{4}, \frac{3}{4}-u, \frac{1}{4}-u; \frac{3}{4}-u, \frac{1}{4}-u, u+\frac{1}{4},$

and 8 similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, with $u=0.083$.

If the other atoms are arranged as follows, a reasonable grouping is obtained that does not conflict with the powder data:

Si: (12k) $\frac{3}{8}0\frac{1}{4}; \frac{1}{8}0\frac{3}{4}; \frac{3}{8}\frac{7}{8}\frac{1}{2}; \frac{3}{8}\frac{1}{8}0; 0\frac{1}{4}\frac{3}{8}; 0\frac{3}{8}\frac{1}{8}; \frac{7}{8}\frac{1}{4}\frac{3}{8}; \frac{5}{8}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{8}0; \frac{1}{8}\frac{5}{8}\frac{1}{2}; \frac{1}{4}\frac{3}{8}\frac{7}{8}; \frac{1}{4}\frac{1}{8}\frac{5}{8}$

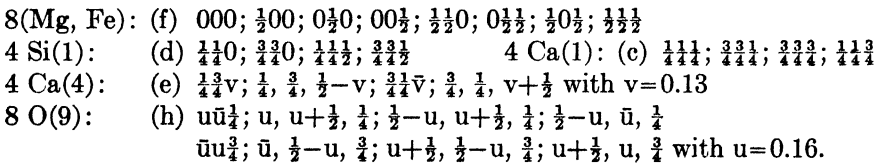
O: xyz; etc. (1930, 352, p. 131) with the parameters $x=-0.035$, $y=0.125$, $z=0.284$. Other values, $x=0.055$, $y=0.11$, $z=0.284$, which cannot be excluded, are thought improbable.

(ap) A structure has been proposed for **euclase**, HBeAlSiO_5 , which explains spectrometric measurements of the first twelve orders of reflection from the (010) face. This arrangement based on C_{2h}^5 , instead of the previously chosen C_{2h}^2 , has all its atoms in general positions: (e) $\pm(xyz)$; $\pm(x, \frac{1}{2}-y, z+\frac{1}{2})$ with the parameters of Table III. It is considered that the y parameters are essentially correct but that those along X and Z are only approximate.

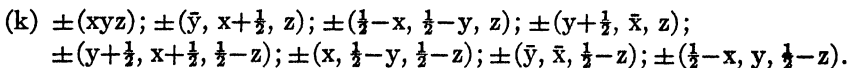
TABLE III. PARAMETERS CHOSEN FOR THE ATOMS OF EUCLASE

Atom	No. per cell	x	y	z
Be	4	0.50	-0.20	0.02
Al	4	.03	-.06	.25
Si	4	.47	.10	.15
O(1)	4	.22	.05	.39
O(2)	4	.26	-.03	-.17
O(3)	4	.54	.19	.37
O(4)	4	-.28	-.15	.11
OH	4	.22	-.17	.31

(aq) A series of spectrometric measurements have been used to give the mineral **vesuvianite** a grouping with four $\text{Ca}_{10}\text{Al}_4(\text{Mg, Fe})_2\text{Si}_9\text{O}_{34}(\text{OH})_4$ molecules in its tetragonal unit. This arrangement, which somewhat resembles that found for the cubic garnets, has atoms in the following general and special positions of D_{4h}^4 :



The remaining atoms are in the following general positions with parameters as listed in Table IV:



The coordinates used in this description are derived from those of 1930, 352, p. 91 by transferring the origin to such a point as $(-\frac{3}{4}, -\frac{1}{4}, \frac{1}{4})$.

It is uncertain how closely this structure describes the atomic arrangement that prevails in vesuvianite crystals. The chosen chemical formula differs from that previously given to the mineral and subsequent studies of the available chemical analyses are said to favor formulas departing appreciably from $\text{Ca}_{10}\text{Al}_4(\text{Mg, Fe})_2\text{Si}_9\text{O}_{34}(\text{OH})_4$. One of these (1932, 294) is $\text{X}_{19}\text{Y}_{18}\text{Si}_{18}(\text{O, OH, F})_{36}$ where $\text{X}=\text{Ca}(\text{Na, etc.})$ and $\text{Y}=(\text{Al, Fe, Mg, etc.})$; another (1933, 461) is $\text{Ca}_6\text{Al}_4(\text{Si, Al})_9(\text{Fe, Mg, etc.})_4(\text{O, OH, F})_{38}$.

TABLE IV. PARAMETERS FOR ATOMS OF VESUVIANITE LYING IN GENERAL POSITIONS

Atom	No. per cell	x	y	z
Si(2)	16	0.19	0.05	0.87
Si(3)	16	.09	-.17	.37
Ca(2)	16	.19	.05	.36
Ca(3)	16	.09	-.17	.88
Al	16	.11	.11	.13
O(1)	16	.22	.17	.08
O(2)	16	.13	.16	.28
O(3)	16	.06	.22	.08
O(4)	16	.07	.13	.48
O(5)	16	.17	.01	.18
O(6)	16	.01	.06	.17
O(7)	16	-.05	.18	.32
O(8)	16	.10	-.08	.07
OH	16	.13	-.25	.06

A, II. Complex Silicate Groups

(ar) The structure found for **hemimorphite**, $\text{H}_2\text{Zn}_2\text{SiO}_5$, indicates that it is a pyrosilicate with a formula best written as $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$. Atoms are in the following positions of C_{2v}^{20} :

- 2 O(1): (a) $00u$; $\frac{1}{2}, \frac{1}{2}, u + \frac{1}{2}$ with $u=0$
 2 H_2O : (b) $\frac{1}{2}0u$; $0, \frac{1}{2}, u + \frac{1}{2}$ with $u=-0.150$
 4 OH: (c) $u0v$; $\bar{u}0v$; $u + \frac{1}{2}, \frac{1}{2}, v + \frac{1}{2}$; $\frac{1}{2} - u, \frac{1}{2}, v + \frac{1}{2}$ with $u=0.75, v=0.350$
 4 O(3): (d) $0uv$; $0\bar{u}v$; $\frac{1}{2}, u + \frac{1}{2}, v + \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2} - u, v + \frac{1}{2}$ with $u=0.187, v=0.305$
 4 Si: (d) $0u'v'$; etc. with $u'=0.160, v'=0$
 8 Zn: (e) xyz ; $\bar{x}\bar{y}z$; $x\bar{y}z$; $\bar{x}yz$, and four similar points about $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (1930, 352, p. 56) with $x=0.300, y=0.342, z=0.010$.
 8 O(2): (e) $x'y'z'$; etc. with $x'=0.161, y'=0.187, z'=0.850$.

In this arrangement a zinc atom is surrounded by three oxygen atoms and one OH group (Figure 327); the water molecules, bounded by OH groups and oxygen atoms lie loosely in big holes that exist in the structure (minimum H_2O to OH or O=ca 3.3 A).

(as) An arrangement has been described for the mineral **bertrandite**, $\text{Be}_2(\text{BeOH})_2\text{SiO}_3\text{SiO}_4$, using spectrometric and photographic data. Based on a hexagonal close packing of oxygen atoms it is said to be intermediate between a silicate chain structure and one having discrete silicate groups. Half the silicon atoms are centers of isolated SiO_4 tetrahedra; the other half form parts of tetrahedra which are linked together in endless SiO_3 chains such as those of diopside. Atoms are placed in special and general positions of C_{2v}^{12} :

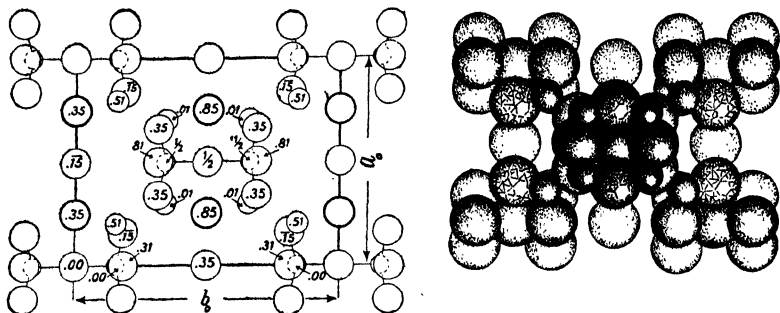


FIG. 327a.—(left) The structure assigned to hemimorphite, $H_2Zn_2SiO_6$, as projected upon the c -face of its orthorhombic unit. The largest circles represent O atoms, H_2O groups and (OH) radicals. The silicate O atoms are joined by light lines with Si (the smallest circles) to form Si_2O_7 groups; the heavily ringed circles are (OH).

FIG. 327b.—(right) A packing drawing of a . The (OH) radicals are line-shaded; the Si atoms cannot be seen.

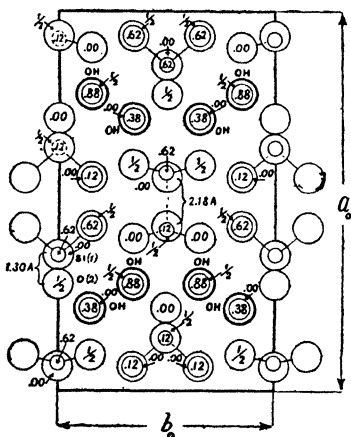


FIG. 328.—The structure proposed for bertrandite, $Be_2(BeOH)_2Si_2O_7$, as projected on the c -face of its orthorhombic unit. The smallest circles are Si, the largest are O atoms [or (OH) if heavily ringed].

TABLE V. PARAMETERS OF THE ATOMS IN BERTRANDITE

Atom	No. per cell	Position	x	y	z
Be(1)	8	(b)	0.215	0.155	0.375
Be(2)	8	(b)	.435	.155	.625
Si(1)	4	(a)	.074	0	.625
Si(2)	4	(a)	.360	0	.625
OH	8	(b)	.215	.155	0
O(1)	4	(a)	.065	0	0
O(2)	4	(a)	.283	0	.50
O(3)	4	(a)	.360	0	0
O(4)	8	(b)	.095	.155	.50
O(5)	8	(b)	.435	.155	.50

TABLE VII. PARAMETERS OF THE ATOMS IN EPIDIDYMIT

Atom	No. per cell	Position	x	y	z
Na(1)	4	(a)	0	0	0
Na(2)	4	(b)	0	$\frac{1}{2}$	0
Be	8	(d)	0.035	0.250	0.052
Si(1)	8	(d)	.065	.200	.060
Si(2)	8	(d)	.435	.200	-.060
Si(3)	8	(d)	.335	.250	.000
OH(1)	4	(c)	-.155	.150	$\frac{1}{2}$
OH(2)	4	(c)	.041	.250	$\frac{1}{2}$
O(1)	8	(d)	.040	.000	.145
O(2)	8	(d)	.040	.500	.145
O(3)	8	(d)	.000	.250	.010
O(4)	8	(d)	.167	.000	-.040
O(5)	8	(d)	.167	.500	-.040
O(6)	8	(d)	.182	.250	.130
O(7)	8	(d)	.318	.250	-.130

C. Two-dimensional Silicate Nets

(aw) The atomic arrangement which has been given to the mica **muscovite**, $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, through a study of photographic and spectrometric intensities is based on C_{2h}^6 (book, p. 343). Approximate parameters of its atoms, all of which except potassium are in general positions, are listed in Table VIII. The central atoms of one quarter of the tetrahedra linked together to produce sheets are aluminum instead of silicon.

(ax) Six **chlorites** with the approximate composition $\text{Al}_2\text{Mg}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$ possess four-molecule monoclinic units having dimensions within the limits $a_0 = 5.304\text{--}5.352$ Å, $b_0 = 9.187\text{--}9.270$ Å, $c_0 = 28.306\text{--}28.582$ Å, $\beta = 97^\circ 9'$. Their space group is considered to be either C_{2h}^3 or C_{2h}^6 . Adopting earlier suggestions that the brittle micas are built up of alternate mica- and brucite-like layers, structures have been assumed and compared with intensities on powder photographs. A grouping with the symmetry of C_{2h}^6 has been preferred but it is obvious that at least until the arrangements based on C_{2h}^3 are definitely eliminated the chlorite structure has not been established.

(ay) Taking the data from powder photographs practically identical structures have been proposed for a **talc**, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, and for **pyrophyllite**, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. The distribution within layers is that previously suggested but the layers are said to be stacked according to the requirements of C_{2h}^6 , not of C_{2h}^3 . Parameters have been proposed but additional confirmation and a more precise description of the arrangement is desirable.

(az) The **clay minerals** with their pronounced micaceous cleavage should have silicon-oxygen tetrahedra united to form sheets. Structures built up of such sheets have been proposed for kaolin, dickite and nacrite,

TABLE VIII. PARAMETERS OF THE ATOMS IN MUSCOVITE

Atom	No. per cell	Position	x	y	z
OH	8	(f)	0.062	0.083	0.055
O(1)	8	(f)	.062	.417	.055
O(2)	8	(f)	.062	.250	.055
O(3)	8	(f)	.478	.083	.164
O(4)	8	(f)	.228	.166	.164
O(5)	8	(f)	.228	.332	.164
(Si+Al)(1)	8	(f)	.033	.417	.135
(Si+Al)(2)	8	(f)	.033	.250	.135
Al	8	(f)	.250	.083	0
K	4	(e)	0	.083	.250

each with the composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. These groupings, based of necessity on powder photographic data and not conclusively proved, are similar; they differ mainly in the orientation of their silicate layers. Each is developed from C_6^4 with all atoms in general positions: (a) xyz ; $x+\frac{1}{2}$, $y+\frac{1}{2}$, z ; x , \bar{y} , $z+\frac{1}{2}$; $x+\frac{1}{2}$, $\frac{1}{2}-y$, $z+\frac{1}{2}$. Kaolin and dickite have four-molecule cells; the unit of nacrite is twice as big. The atomic parameters are listed in Tables IX and X. Other arrangements for both kaolin and dickite are in almost equally good agreement with the data. It is suggested that some samples may have these alternative groupings—or one which combines both. The mineral anauxite resembles kaolin but contains a greater amount of silicon. If this silicon replaces aluminum, as has been proposed, it would have a hitherto unknown six-fold coordination.

Some measurements have indicated that the substance called montmorillonite has an orthorhombic cell similar in size and shape to the monoclinic cell of kaolin (1933, 205).

(ba) **Apophyllite** is a mineral which is sometimes considered a zeolite, sometimes more nearly a mica. Some water can be driven from it without

TABLE IX. ATOMIC PARAMETERS FOR KAOLIN AND DICKITE

Atom	Kaolin			Dickite		
	x	y	z	x	y	z
Al(1)	0.25	-0.17	0	0.25	0.41	0
Al(2)	.25	.17	0	.25	.08	0
Si(1)	.01	.50	0.19	.14	.25	0.19
Si(2)	.01	.17	.19	-.36	.08	.19
O(1)	-.05	.50	.08	.11	.25	.08
O(2)	-.05	.17	.08	-.39	.08	.08
O(3)	.03	.33	.23	.16	.42	.23
O(4)	.28	-.41	.23	.41	.17	.23
O(5)	.28	.08	.23	-.09	.17	.23
OH(1)	-.05	-.17	.08	-.39	.42	.08
OH(2)	-.05	0	.42	-.11	.25	.42
OH(3)	-.45	.17	.42	.39	.08	.42
OH(4)	.05	.33	.42	.39	.42	.42

shown that dehydration does not seriously alter the observed powder pattern of this zeolite.

(bc) The structure found for **natrolite** from photographic spectral data has the symmetry of C_{2v}^{19} and contains eight molecules of the composition $Na_2Al_2Si_3O_{10} \cdot 2H_2O$. All atoms except one set of silicon are in general positions (1930, 352, p. 55):

(b) $xyz; \bar{x}\bar{y}z; x+\frac{1}{4}, \frac{1}{4}-y, z+\frac{1}{4}; \frac{1}{4}-x, y+\frac{1}{4}, z+\frac{1}{4}$ and three sets of similar points about $\frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$.

The parameters of these atoms are listed in Table XI. Si(1) atoms are in special positions (a) 00u; etc. with $u=0$; i.e. at the points 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$. The nature of the tetrahedral network and the positions occupied by water molecules can be seen from Figure 329.

Besides closely agreeing determinations of cell dimensions on natural natrolites from several sources, cell data exist on four synthetic compounds of this type (Table XII).

TABLE XI. PARAMETERS FOR ATOMS OF NATROLITE LYING IN GENERAL POSITIONS

Atom	No. per cell	x	y	z
Na	16	0.222	0.028	0.625
Al	16	.036	.089	.625
Si(2)	16	.153	.208	.625
O(1)	16	.069	.180	.625
O(2)	16	.014	.067	.875
O(3)	16	.183	.236	.375
O(4)	16	.097	.042	.500
O(5)	16	.208	.153	.750
H ₂ O	16	.069	.180	.125

FIG. 329.—A projection upon its c-face of one eighth of the unit of natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$. The small light circles are Si, the ringed small circles are Al atoms. Na atoms are shown by circles of intermediate size; the largest ringed circles are H₂O molecules.

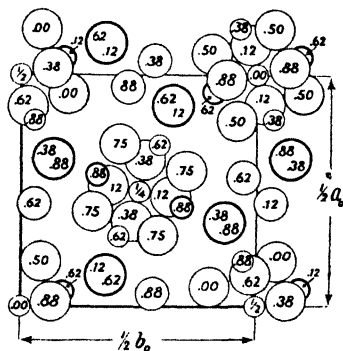


TABLE XII. CELL DIMENSIONS ON SUBSTITUTED NATROLITES

Compound	a_0	b_0	c_0
$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	18.3	18.6	6.57
$Li_2Al_2Si_3O_{10} \cdot 2H_2O$	18.0	18.6	6.5
$Ag_2Al_2Si_3O_{10} \cdot 2H_2O$	18.6	18.9	6.6
$(NH_4)_2Al_2Si_3O_{10}$ anhydrous	17.9	18.4	6.6

(bd) The X-ray patterns of *scolecite*, $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$, are indistinguishable from those of *natrolite* so that it must have a unit of practically the same size and shape. Earlier it was suggested (1930, 258) that $\text{Ca}+3\text{H}_2\text{O}$ of *scolecite* replace $2\text{Na}+2\text{H}_2\text{O}$ of *natrolite*. A recent study proposes instead that Ca atoms in the former occupy half the Na positions in *natrolite* leaving the other half vacant and that the eight new H_2O molecules go into half the 16-fold unoccupied holes in the *natrolite* structure with the approximate parameters $x=0.22$, $y=0.028$, $z=0.125$. No data are available for distinguishing between these possibilities.

(be) *Mesolite*, $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30}\cdot 8\text{H}_2\text{O}$, is another zeolite which gives a pattern nearly identical with that of *natrolite*. The large cell of Table I is indicated by certain faint lines seen on some rotation photographs.

(bf) Data from spectral photographs have been used to assign an atomic arrangement to the rhombohedral zeolite *chabazite*. The atoms of the two $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$ molecules are in the following positions of D_{3d}^5 :

- 2 Ca: (c) $\pm(uuu)$ with $u=0.17$
 6 O(1): (f) $\pm(u\bar{u}0)$; $\pm(\bar{u}0u)$; $\pm(0u\bar{u})$ with $u=0.34$
 6 O(2): (g) $\pm(u\bar{u}\frac{1}{2})$; $\pm(\bar{u}\frac{1}{2}u)$; $\pm(\frac{1}{2}u\bar{u})$ with $u=0.14$
 6 O(3): (h) $\pm(uuv)$; $\pm(uvu)$; $\pm(vuu)$ with $u=0.35$, $v=-0.02$
 6 O(4): (h) $u'u'v'$ with $u'=0.13$, $v'=0.50$
 $\text{H}_2\text{O}(1)$: (h) $u_1u_1v_1$ with $u_1=0.31$, $v_1=0.70$
 $\text{H}_2\text{O}(2)$: (h) $u_2u_2v_2$ with $u_2=0.14$, $v_2=-0.08$
 (Si+Al): (i) $\pm(xyz)$; $\pm(yzx)$; $\pm(zxy)$; $\pm(yxz)$; $\pm(xzy)$; $\pm(zyx)$

with $x=0.23$, $y=0.44$, $z=-0.01$.

X-ray studies have been made of the dehydration of *chabazite*. It has also been shown that mercury can replace the water in this zeolite without destroying its diffraction pattern; by one investigator (1932, 286) this has been taken to mean that the water molecules do not occupy definite positions within the *chabazite* structure.

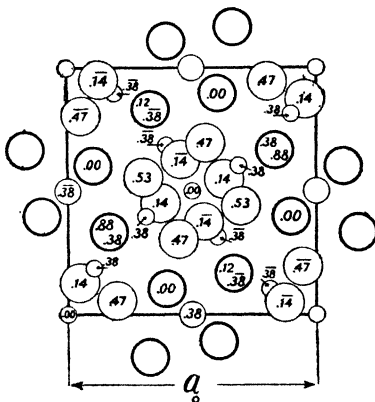
(bg) Another zeolite to which an atomic arrangement has been assigned is *edingtonite*, $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20}\cdot 8\text{H}_2\text{O}$. There is some uncertainty as to the true symmetry of this mineral. Samples of Swedish origin have been found to be orthorhombic with $a_0=9.56$ A, $b_0=9.68$ A, $c_0=6.53$ A; their space group has been reported as V^3 . Material from Old Kilpatrick, Scotland with the cell dimensions of Table I is said to be completely tetragonal.

The Laue photographs of *edingtonite* from Böhlet, Sweden are apparently tetragonal. Proceeding on the assumption that its atomic arrangement does not depart significantly from this higher symmetry, photographic spectral data have been used to place its two molecules in the following special and general positions of V_d^3 (1930, 352, p. 74):

Ba:	(c) $0\frac{1}{2}u$; $\frac{1}{2}0\bar{u}$ with $u=0.375$	(Al+Si)(1):	(a) 000 ; $\frac{1}{2}\frac{1}{2}0$
H ₂ O(1):	(e) u , $\frac{1}{2}-u$, v ; $\frac{1}{2}-u$, \bar{u} , \bar{v} ; \bar{u} , $u+\frac{1}{2}$, v ; $u+\frac{1}{2}$, u , \bar{v} with $u=0.333$, $v=0.875$		
H ₂ O(2):	(e) u' , $\frac{1}{2}-u'$, v' with $u'=0.103$, $v'=0$		
O(1):	(e) u_1 , $\frac{1}{2}-u_1$, v_1 with $u_1=0.333$, $v_1=0.375$		
O(2):	(f) xyz ; $y\bar{x}\bar{z}$; $\bar{x}\bar{y}z$; $\bar{y}x\bar{z}$; $\frac{1}{2}-x$, $y+\frac{1}{2}$, \bar{z} ; $\frac{1}{2}-y$, $\frac{1}{2}-x$, z ; $x+\frac{1}{2}$, $\frac{1}{2}-y$, \bar{z} ; $y+\frac{1}{2}$, $x+\frac{1}{2}$, z with $x=0.055$, $y=0.194$, $z=0.472$		
O(3):	(f) $x_1y_1z_1$ with $x_1=0.128$, $y_1=0.047$, $z_1=0.139$		
(Al+Si)(2):	(f) $x'y'z'$ with $x'=0.186$, $y'=0.103$, $z'=0.375$.		

The similarity between the tetrahedral strings in this mineral and in other zeolites can be seen by comparing Figure 330 with Figure 329 for natrolite. In this edingtonite arrangement four H₂O molecules are coordinated about each barium atom. The positions chosen for water are considered most probable but because of the heavy barium the available X-ray data cannot locate them uniquely.

FIG. 330.—A basal projection of the tetragonal structure given to edingtonite, Ba₂Al₄Si₆O₂₀·8H₂O. Al and Si atoms, which are not separately determined, are the smallest circles; intermediate circles are Ba. Molecules of H₂O are heavily ringed.



(*bh*) The true unit prism of thomsonite, NaCa₂Al₆Si₆O₂₀·6H₂O, contains four molecules (Table I). There is, however, an approximate halving along the *c* direction that suggests a two-molecule pseudo-unit. A structure based on this pseudo-cell with its atoms in the following positions of V_h^7 is thought to be approximately correct.

Ca:	(c) $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$
(2 Ca+2 Na):	(h) $\pm(u0v)$; $\pm(\frac{1}{2}-u, \frac{1}{2}, v)$ with $u=0.069$, $v=0.25$
(2 Si+2 Al):	(g) $\pm(\frac{1}{4}\frac{1}{4}u)$; $\pm(\frac{3}{4}\frac{1}{4}\bar{u})$ with $u=0.875$
H ₂ O(1):	(e) $\pm(0u0)$; $\pm(\frac{1}{2}, \frac{1}{2}-u, 0)$ with $u=0.139$
H ₂ O(2):	(h) u_10v_1 with $u_1=0.403$, $v_1=0.75$
H ₂ O(3):	(h) u_20v_2 with $u_2=0.111$, $v_2=0.75$
O(1):	(f) $\pm(\frac{1}{2}u\frac{1}{2})$; $\pm(0, u+\frac{1}{2}, \frac{1}{2})$ with $u=0.361$
O(2):	(h) $u'0v'$ with $u'=0.402$, $v'=0.25$.

TABLE XIII. PARAMETERS FOR ATOMS OF THOMSONITE LYING IN GENERAL POSITIONS

Atom	No. per cell	x	y	z
O(3)	8	0.167	0.194	0.75
O(4)	8	.180	.119	.375
O(5)	8	.305	.139	0
O(6)	8	.375	.194	.375
(Si+Al)(2)	8	.125	.194	.500
(Al+Si)(3)	8	.305	.125	.250

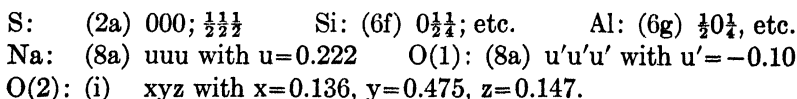
The rest of the atoms are in general positions: (i) $\pm(xyz)$; $\pm(x\bar{y}z)$; $\pm(\frac{1}{2}-x, \frac{1}{2}-y, z)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, \bar{z})$, with the parameters of Table XIII. It has been suggested that this simplified structure departs from the true one mainly in the distribution of Al and Si atoms within the positions assigned to them as centers of oxygen tetrahedra. The existing data are inadequate to show whether this is the case.

The axes of this description (abc) are connected with those of 1930, 352, p. 61 ($X'Y'Z'$) by the relations: $a=Z'$, $b=X'$, $c=Y'$.

(bi) X-ray patterns have been made of partially dehydrated heulandite and of the β -heulandite obtained by dehydrating above 210° C. The former gives a heulandite-like pattern and takes up water reversibly. The β -form cannot be reversed. Digestion of heulandite in HCl results in a silica which, though pseudomorphic after the original crystal, yields an amorphous X-ray pattern.

(bj) Other minerals which have been found to have three-dimensional linked SiO_4 and AlO_4 tetrahedral networks are members of the **sodalite** group.

A structure for sodalite itself, $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$, has already been proposed [(x) book, p. 352]. This was developed from the space group T_d^4 . Similar arrangements have been suggested for haüynite and noselite. Writing the formula for haüynite as essentially $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{SO}_4$ with some substitution of calcium for sodium, the necessary atomic positions, already listed for sodalite, [(x) book, p. 352], are:



The coordinates for noselite are nearly identical, the assumption being made that only some of the sulfate positions centering about 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ are occupied. For Na, $u=0.217$; for O(1), $u'=-0.100$; for O(2), $x=0.136$, $y=0.475$, $z=0.147$.

A debate over the true formula of haüynite has led to another, but closely related, structure based on T_d^4 . Considering this mineral to be a solid solution of the composition $(\text{Na}, \text{Ca})_{4-3}\text{Al}_3\text{Si}_3\text{O}_{24} \cdot (\text{SO}_4)_{1-2}$, sodalite

TABLE XIV. THE T_d^1 STRUCTURES FOR SODALITE AND NOSELITE

Arrangement	Sodalite		Noselite	
	Atom	Parameters	Atom	Parameters
(1a) 000	Cl	—	S	—
(1b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Cl	—	—	—
(12f) $u0\frac{1}{2}$; etc.	(6Al+6Si)	$u=0.25$	(6Al+6Si)	$u=0.25$
(4a) uuu ; etc.	Na(1)	$u=0.175$	Na(1)	$u=0.150$
(4a) $u'u'u'$; etc.	Na(2)	$u'=0.675$	Na(2)	$u'=0.750$
(4a) $u_1u_1u_1$; etc.	—	—	O(1)	$u_1=0.897$
(12g) uuv ; etc.	O(1)	$u=0.147$ $v=0.445$	O(2)	$u=0.144$ $v=0.473$
(12g) $u'u'v'$; etc.	O(2)	$u'=0.660$ $v'=-0.056$	O(3)	$u'=0.645$ $v'=-0.028$

(4a): uuu ; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$
(12f): $u0\frac{1}{2}$; $\bar{u}0\frac{1}{2}$; $u\frac{1}{2}0$; $\bar{u}\frac{1}{2}0$; $\frac{1}{2}u0$; $\frac{1}{2}\bar{u}0$; $0u\frac{1}{2}$; $0\bar{u}\frac{1}{2}$; $0\frac{1}{2}u$; $0\frac{1}{2}\bar{u}$; $\frac{1}{2}0u$; $\frac{1}{2}0\bar{u}$
(12g): uuv ; $u\bar{u}\bar{v}$; $\bar{u}u\bar{v}$; $\bar{u}\bar{u}v$; vuu ; $\bar{v}u\bar{u}$; $\bar{v}\bar{u}u$; $v\bar{u}\bar{u}$; uvu ; $\bar{u}\bar{v}u$; $u\bar{v}\bar{u}$.

and noselite have been assigned the groupings of Table XIV. Upon this basis some but not all cells of haüynite would contain SO_4 groups in approximately the positions (1b) and (4a) [for O(1)] of noselite; Ca would replace Na(1) or Na(2). A convincing choice between these alternative arrangements cannot be made from the existing X-ray data.

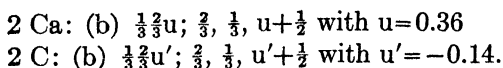
It has been found that the two minerals ittnerite and skolopseite (1934, 162) give weak haüynite patterns and presumably are alteration products.

None of these more recent studies of substances related to the ultramarines (*aa*) gives support to the suggestion earlier advanced that their alkali atoms are "wandering" without fixed positions in the structure.

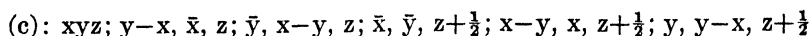
(*bk*) The following structure, which gives qualitative agreement with the data from two oscillation photographs, has been proposed for zunyite, $Al_{18}Si_6O_{20}(OH, F)_{18}Cl$. Based on T_d^2 it places four molecules within the unit cube. Atoms are in points having the coordinates listed below and in three similar sets of points (1930, 352, p. 128) about $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

Cl:	(4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Si: (4d) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$	Al(1): (4e) $\frac{3}{4}\frac{3}{4}\frac{3}{4}$
Si:	(16a) uuu ; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$ with $u=0.117$		
O(1):	(16a) $u_1u_1u_1$ with $u_1=-0.177$		
O(2):	(16a) $u_2u_2u_2$ with $u_2=0.184$		
(OH, F)(1):	(24a) $u00$; $\bar{u}00$; $0u0$; $0\bar{u}0$; $00u$; $00\bar{u}$ with $u=0.273$		
(OH, F)(2):	(48d) uuv ; $u\bar{u}\bar{v}$; $\bar{u}u\bar{v}$; $\bar{u}\bar{u}v$; vuu ; $\bar{v}u\bar{u}$; $\bar{v}\bar{u}u$; $v\bar{u}\bar{u}$; uvu ; $\bar{u}\bar{v}u$; $u\bar{v}\bar{u}$; $\bar{u}v\bar{u}$ with $u=0.181$, $v=0.545$		
O(3):	(48d) $u'u'v'$ with $u'=0.139$, $v'=0.006$		
Al(2):	(48d) $u_1u_1v_1$ with $u_1=0.089$, $v_1=-0.228$.		

(*bl*) The hexagonal unit of cancrinite contains one molecule whose ideal composition is said to be $Ca_2Na_6Al_6Si_6O_{24}\cdot 2CO_3$. An arrangement which is compared with some estimated intensity data from rotation photographs has been developed from C_6^6 . It is as follows:



The rest of the atoms are in general positions:

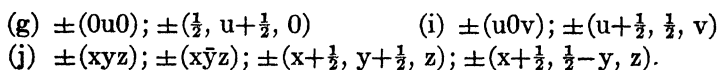


with the parameters of Table XV.

TABLE XV. PARAMETERS FOR ATOMS OF CANCRINITE
 LYING IN GENERAL POSITIONS

Atom	No. per cell	x	y	z
Na	6	0.50	0.50	0.22
Si	6	.03	.26	.26
Al	6	.26	.23	.24
O(1)	6	.05	.36	.01
O(2)	6	.36	.32	-.03
O(3)	6	.17	.27	.26
O(4)	6	-.13	.16	.24
O(5)	6	.20	.64	.36

(*bm*) The **feldspars** have a grouping which thus far has resisted complete analysis. A few years ago (1929, 289a; 1931, 391) a type of structure was proposed which did not provide reasonable interatomic distances. Recently a different arrangement has been suggested for a sanidine ($KAlSi_3O_8$, with some Na replacing K). This gives approximately the right atomic separations and is in fairly good agreement with the reflections on several rotation photographs. It has atoms in the following special and general positions of C_{2h}^3 with the parameters of Table XVI:



A projection of the unit cell on its *ac*-plane is reproduced in Figure 331. Its interlocking network of (Al, Si) O_4 tetrahedra is seen to be very different from those deduced for the sodalite and zeolitic minerals.

Measurements upon celsian, $BaAl_2Si_2O_8$, have indicated that it is triclinic but that it probably does not depart far from the monoclinic arrange-

TABLE XVI. PARAMETERS OF THE ATOMS IN SANIDINE

Atom	No. per cell	Position	x	y	z
O(1)	4	(g)	0	0.139	0
O(2)	4	(i)	0.658	0	0.236
O(3)	8	(j)	.819	.153	.236
O(4)	8	(j)	.000	.319	.250
O(5)	8	(j)	.153	.125	.417
Si+Al(1)	8	(j)	.000	.186	.217
Si+Al(2)	8	(j)	.703	.111	.347
K	4	(i)	.294	0	.139

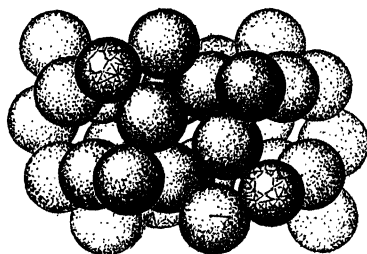
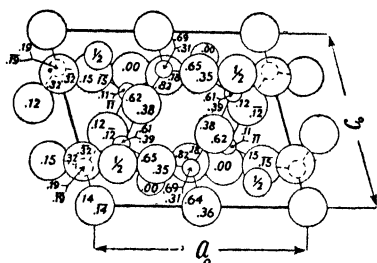


FIG. 331a.—(left) A portion of the monoclinic structure found for sanidine, KAlSi_3O_8 , as projected on its b -face. The smallest circles are Al or Si (not distinguished in the structure), the largest are O atoms.

FIG. 331b.—(right) A packing drawing of a . The K ions are line-shaded; two of the (Si, Al) atoms are visible as black spheres.

ment of sanidine. The K-Ba feldspars, adularia and hyalophane, containing up to ca 15% BaO are truly monoclinic. In these minerals there is thought to be a haphazard replacement of K and Si by Ba and Al.

The soda feldspar albite, $\text{NaAlSi}_3\text{O}_8$, though definitely triclinic can be described in terms of a sanidine-like cell. It has been found that an arrangement with parameters modified from those of KAlSi_3O_8 yields fairly satisfactory agreement with photographic data. The cell for this description, being base-centered and hence not the simplest one possible has for its general positions the coordinates: (i) $\pm(xyz)$; $\pm(x+\frac{1}{2}, y+\frac{1}{2}, z)$. Its parameters are recorded in Table XVII. The similarity between this structure and the sanidine grouping is best seen by comparing this table with Table XVI.

TABLE XVII. PARAMETERS OF THE ATOMS IN ALBITE

Atom	x	y	z
O(1)	0.014	0.125	-0.014
O(2)	.611	-.014	.278
O(3, a)	.833	.125	.214
O(3, b)	.311	.361	.250
O(4, a)	.014	.305	.264
O(4, b)	.536	.194	.230
O(5, a)	.194	.139	.389
O(5, b)	.658	.389	.411
Si+Al(1, a)	.000	.175	.222
Si+Al(1, b)	.472	.328	.233
Si+Al(2, a)	.714	.105	.333
Si+Al(2, b)	.214	.383	.361
Na	.278	-.167	.172

All of the plagioclase feldspars do not have albite-like cells. The units of two andesites with albite-anorthite ratios of 3:1 and 2:1 are like albite, but anorthite itself, $\text{CaAl}_2\text{Si}_2\text{O}_8$, and a labradorite with the ratio 1:1 both have c_0 axes that are twice as long.

New data bearing on the cell dimensions of the feldspars are assembled in Table XVIII (cf. Table XVIII, p. 354 of book).

TABLE XVIII. NEW CELL DIMENSIONS ON FELDSPARS

<i>Mineral</i>	<i>Symmetry</i>	a_0	b_0	c_0	α	β	γ
Sanidine	Monoclinic	8.45	12.90	7.15	—	116°6'	—
Adularia	Monoclinic	8.45	12.90	7.15	—	116°3'	—
Hyalophane (A, B)	Monoclinic	8.45	12.90	7.15	—	115°35'	—
Hyalophane (C)	Monoclinic	8.52	12.95	7.14	—	115°35'	—
Celsian	Triclinic	8.63	13.10	7.29	ca 90°	116°	ca 90°
Albite	Triclinic	8.14	12.86	7.17	94°3'	116°29'	88°9'
Andesite	Triclinic	8.14	12.86	7.17	93°23'	116°28'	89°59'
Labradorite	Triclinic	8.21	12.95	14.16	93°31'	116°3'	89°55'
Anorthite	Triclinic	8.21	12.95	14.16	93°13'	115°56'	91°12'

(bn) An earlier (1929, 115) study of wollastonite, CaSiO_3 , resulted in a monoclinic unit. More recently it has been shown to be triclinic. Similar cells can be given to pectolite, $\text{NaHCa}_2(\text{SiO}_3)_3$, and probably to schizolite, $\text{HNa}(\text{Ca, Mn})_2(\text{SiO}_3)_3$.

(bo) The cell dimensions for epidote quoted in Table I are those of 1932, 172. The two earlier studies gave it a two-molecule unit with a_0 half as long. Clinozoisite, an epidote without iron, is structurally like the ordinary variety.

(bp) The structure of nephelite is yet to be determined. A few suggestions have been made but, unsupported by the necessary X-ray data, they are of little value.

(bq) Unit cells have been assigned to two wöhlerite-like minerals besides the one quoted in Table I. Lavenite with 20% of its Zr replaced by Ca_2 has $a_0=10.93$ A, $b_0=9.99$ A, $c_0=7.18$ A, $\beta=110^\circ28'$; hiortdahlite with Ca_2 substituting for 25% of its (Zr, F)Na is reported to be triclinic but with very similar cell dimensions: $a_0=10.91$ A, $b_0=10.29$ A, $c_0=7.32$ A, $\alpha=90^\circ29'$, $\beta=108^\circ50'$, $\gamma=90^\circ8'$.

(br) Mosandrite is a rinkite in which H and OH replace Na and F atoms. Though monoclinic the cell dimensions found for it are nearly the same as those given to the orthorhombic rinkite. They are $a_0=18.47$ A, $b_0=5.67$ A, $c_0=7.46$ A, $\beta=91^\circ13'$.

(bs) The unit cubes of several garnets have been measured. One, a 48% grossularite-andradite, 52% almandite-pyrope, has $a_0=11.668$ A (1933, 182). Spessartite gives 11.603 A; partschinite, a spessartite with

some iron in place of manganese has $a_0 = 11.613 \text{ \AA}$ (1933, 522). It has also been found that a_0 for Ca-Fe garnets increases from 11.93 \AA to 12.14 \AA as the titanium content mounts from zero.

(*bt*) It is suggested that though they seemingly are tetragonal, the **scapolites** really are complex twinings of monoclinic and triclinic individuals.

Chapter XXA. Structures of Organic Compounds

Nearly all the X-ray studies of organic crystals being published are limited to unit cell and space group determinations. Some, as indicated in the large tables, prove molecular symmetry for suitably constituted compounds. Others point to the existence of associated molecules in the crystalline state. Though a few of these associations, marked A in the tables, may be real most of them are to be explained by the choice of too large a unit cell.

Some progress has been made towards an understanding of the atomic arrangements in aliphatic structures but most of the increase in our knowledge of atomic positions in organic crystals has come through the investigation of several aromatic hydrocarbons.

A. The Structures of Organic Salts and of Metallo-organic Compounds

(*bd*) A previous study of $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ has indicated that the eight molecules in its unit cube are arranged according to the requirements of T_h^4 . This has been confirmed and it has been shown that by placing atoms in the following positions of this space group an arrangement is obtained which yields plausible interatomic distances and does not conflict with data from Laue and oscillation photographs.

Be: (32b) uuu ; etc. [see XVIII A, (*ce*)] with $u = -0.060$
O(1): (8f) 000 ; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$
O(2): (g) xyz ; etc. with $x = -0.163$, $y = -0.064$, $z = -0.038$
C(1): (48c) u_100 ; etc. with $u_1 = 0.197$
C(2): (48c) $u'00$; etc. with $u' = 0.295$.

As was earlier pointed out this choice of space group implies that the two oxygen atoms of the acetate group are geometrically equivalent.

(*be*) Two studies of the dihydrate of copper formate, $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, differ both in the size of the unit and in the chosen space group.

(*bf*) It is said that the lead atoms in $\text{Pb}(\text{HCOO})_2$ have the coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$; $\frac{1}{2}, \frac{3}{2}, \frac{1}{2}$; $\frac{3}{2}, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $\frac{3}{2}, \frac{3}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{3}{2}, \frac{3}{2}$; $\frac{3}{2}, \frac{1}{2}, \frac{3}{2}$.

TABLE I. THE CRYSTAL STRUCTURES OF ORGANIC SALTS AND METALLO-ORGANIC COMPOUNDS

<i>Substance, symmetry and type</i>	<i>Space group</i>	<i>No. mol. per cell</i>	<i>Min. mol. symmetry</i>	<i>a₀</i>	<i>b₀</i>	<i>c₀</i>	<i>References</i>
Silver Nitrate Urea AgNO ₃ ·CO(NH ₂) ₂	Mon.	8	A	10.23	16.84 β=77°	6.25	1934, 55.
Mellite Al ₂ C ₁₂ O ₁₂ ·18H ₂ O	Tet.	16		22.0		23.3	1933, 31.
Barium Chloride Glycine BaCl ₂ ·2CH ₂ NH ₂ COOH	Ort.	4	C ₁ or C ₂	7.96	14.7	9.21	1933, 41.
Beryllium Oxacetate BeO(C ₂ H ₃ O ₂) ₂	Cub. (j), (bd)						1934, 206.
Triphenyl Bismuthine Dichloride Ort.	V ²	8	A	17.31	22.39	9.20	1931, 138.
Calcium Sulfate Urea CaSO ₄ ·CO(NH ₂) ₂	Tri.	4	A	14.74	14.95	6.47	1933, 179.
Cesium Acid Tartrate CsHC ₄ H ₄ O ₆	Ort.	4		α=91°26', β=90°22', γ=86°42' 7.66	11.58	8.03	1931, 169.
Copper Formate Dihydrate Cu(HCO ₂) ₂ ·2H ₂ O	Mon. (be)						1931, 241, 364.
Copper Formate Tetrahydrate Cu(HCO ₂) ₂ ·4H ₂ O	Mon.						1931, 241.
Cuprous Glutathione Ort.	V ⁴	4		28.0	8.74	5.57	1932, 366.
Potassium Acid Tartrate KHC ₄ H ₄ O ₆	Ort.	4		7.614	10.70	7.80	1932, 147.
Rochelle Salt NaOOC(CHOH) ₂ COOK·4H ₂ O	Ort.	4		11.913	14.324	6.153	1933, 444.
Lead Formate Pb(HCO ₂) ₂	Ort. (b), (bf)						1932, 190.

Substance, symmetry and type	Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
Bisethylene Diamino Platinous Chloride $\text{Pt}(\text{C}_2\text{H}_5\text{N}_2)_2\text{Cl}_2$ Tri.	C_i^1	1		8.37	4.95	6.86	1933, 109.
α -Bisdiethyl Sulfine Platinous Chloride Mon.		2		12.0	7.9	7.7	1934, 61.
α -Bisdimethyl Sulfine Platinous Chloride $\text{Pt}[\text{S}(\text{CH}_3)_2]_2\text{Cl}_2$ Mon.	C_{2h}^2 or C_{2h}^3	2		10.16	6.01	8.48	1934, 61.
β -Bisdimethyl Sulfine Platinous Chloride $\text{Pt}[\text{S}(\text{CH}_3)_2]_2\text{Cl}_2$ Mon.		4		9.3	13.2	8.7	1934, 61.
Methyl Silicate $(\text{CH}_3)_4\text{SiO}_4$	T^1	4	C_4	9.85 at -80°C (?)	$\beta=105^\circ$		1931, 106.
Dimethyl Thallium Bromide $\text{Tl}(\text{CH}_3)_2\text{Br}$	D_{4h}^{17}	2	D_4^h	4.47		13.78	1934, 217.
Dimethyl Thallium Chloride $\text{Tl}(\text{CH}_3)_2\text{Cl}$	D_{4h}^{17}	2	D_4^h	4.29		14.01	1934, 217.
Dimethyl Thallium Iodide $\text{Tl}(\text{CH}_3)_2\text{I}$	D_{4h}^{17}	2	D_4^h	4.78		13.43	1934, 217.

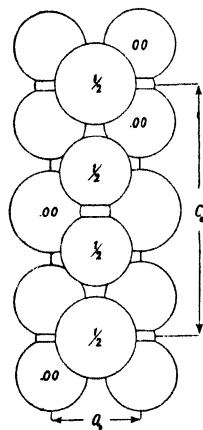


FIG. 332.—A projection upon one of its a -faces of atoms in the tetragonal arrangement deduced for $\text{Tl}(\text{CH}_3)_2\text{I}$. The largest circles are I ions, the slightly smaller ones are CH_3 groups. The sizes used in this drawing are determined by the results on the methyl substituted ammonium salts.

(bg) An elaborate discussion, based on powder photographs, has been given of possible arrangements for the atoms in **methyl silicate**, $(\text{CH}_3)_4\text{SiO}_4$. It was shown that the structure is based on T^1 but the correct grouping was not definitely established.

(bh) Spectral photographs have been used to find an atomic arrangement for the atoms in **dimethyl thallium iodide**, $\text{Tl}(\text{CH}_3)_2\text{I}$. They are in the following special positions of D_{4h}^{17} :

$$\begin{array}{ll} 2 \text{ Tl:} & \text{(a) } 000; \frac{1}{2}\frac{1}{2}\frac{1}{2} \\ 4(\text{CH}_3): & \text{(e) } 00u; 00\bar{u}; \frac{1}{2}, \frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u \text{ with } u=ca \text{ } 0.15. \end{array} \quad \begin{array}{l} 2 \text{ I:} \\ \text{(b) } \frac{1}{2}\frac{1}{2}0; 00\frac{1}{2} \end{array}$$

The $\text{Tl}-\text{CH}_3$ separation is 2.01 Å; the distance between CH_3 groups through which contact is made along c , is 4.17 Å (Figure 332). This large CH_3-CH_3 separation may mean that u should be greater than 0.15.

The bromide and chloride are structurally isomorphous with the iodide but the methyl parameter could not be found for them.

B. The Structures of Substituted Ammonium Salts

(bi) Quantitative spectrometer measurements have been used to find the structure of **dimethyl ammonium chlorostannate**, $[\text{NH}_2(\text{CH}_3)_2]_2\text{SnCl}_6$. Atoms are in special and general positions of C_{2v}^7 :

$$\text{(a) } 0uv; \frac{1}{2}, \bar{u}, v+\frac{1}{2} \quad \text{(b) } xyz; \frac{1}{2}-x, \bar{y}, z+\frac{1}{2}; x+\frac{1}{2}, \bar{y}, z+\frac{1}{2}; \bar{x}yz$$

TABLE II. THE CRYSTAL STRUCTURES OF SUBSTITUTED AMMONIUM SALTS

Substance, symmetry and structure type	a_0	b_0	c_0	No. mol. per cell	References	
Monomethyl Ammonium Cupric Chloride $(\text{NH}_2\text{CH}_3)_2\text{CuCl}_4$	Ort.	7.30	7.535	18.55	4	1933, 157.
Dimethyl Ammonium Chlorostannate $[\text{NH}_2(\text{CH}_3)_2]_2\text{SnCl}_6$	Ort. (bi)	7.26	14.28	7.38	2	1933, 157; 1934, 60.
Tetramethyl Ammonium Fluosilicate $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$	Tet. (bj)	7.88		11.19	2	1934, 57.
n-Monoamyl Ammonium Chloride $n\text{-C}_8\text{H}_{11}\text{NH}_3\text{Cl}$	Tet. (bk)	7.03 at -80° C		16.70	4	1933, 438.
Octadecyl Ammonium Chloride $\text{C}_{18}\text{H}_{37}\text{NH}_3\text{Cl}$	Ort. (bl)	5.45	5.40	69.4	4	1932, 41, 42.

with the parameters of Table III. The axes of this description, $XYZ=abc$, are connected with those used for an earlier crystallographic description, $a'b'c'$, by the relations $X=a=a'$, $Y=b=c'$, $Z=c=b'$.

TABLE III. PARAMETERS OF THE ATOMS IN $[(\text{CH}_3)_2\text{NH}_2]_2\text{SnCl}_6$

Atom	No. per cell	Position	x	y	z
Sn	2	(a)	0	0.250	0
Cl(1)	2	(a)	0	.390	0.180
Cl(2)	2	(a)	0	.110	-.180
Cl(3)	4	(b)	0.235	.185	.190
Cl(4)	4	(b)	.235	.315	-.190
N(1)	2	(a)	0	.620	.690
N(2)	2	(a)	0	.880	.310
CH ₃ (1)	2	(a)	0	.605	.875
CH ₃ (2)	2	(a)	0	.895	.125
CH ₃ (3)	2	(a)	0	.530	.625
CH ₃ (4)	2	(a)	0	.970	.375

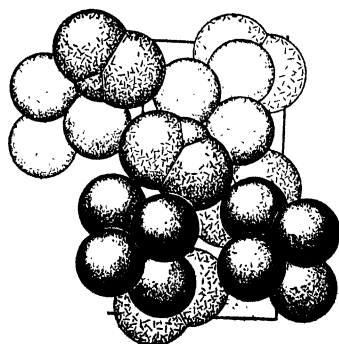
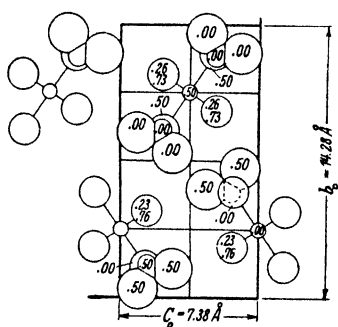


FIG. 333a.—(left) A portion of the structure of $[\text{NH}_2(\text{CH}_3)_2]_2\text{SnCl}_6$ projected on the a -face of its orthorhombic cell. The segments of circles, representing NH_2 , join CH_3 groups (largest circles). The Cl and Sn (smallest circles) of SnCl_6 ions are connected by light lines.

FIG. 333b.—(right) A packing drawing of a . The $\text{NH}_2(\text{CH}_3)_2$ ions are line-shaded. Atoms of Sn cannot be seen.

The substituted ammonium chlorostannates thus far analyzed have been relatively simple distortions of the $(\text{NH}_4)_2\text{PtCl}_6$ grouping [XVII, (a)]. This arrangement (Figure 333) can be similarly viewed but the distortion is great. The two C-N bonds of a $(\text{CH}_3)_2\text{NH}_2^+$ ion make the tetrahedral angle with one another; the $\text{CH}_3\text{-Cl}$ separation, ca 3.83 Å, is the same as that found in other substituted ammonium chlorostannates.

(b) The tetragonal packing found for the atoms in tetramethyl ammonium fluosilicate, $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$, is a distortion of that prevailing in the cubic $[\text{N}(\text{CH}_3)_4]_2\text{SnCl}_6$ (u). Atoms are in the following general and special positions (1930, 352, p. 82) of C_{4h}^6 with parameters fixed by a series of spectrometric measurements (Figure 334):

TABLE IV. THE CRYSTAL STRUCTURES OF ALIPHATIC ORGANIC COMPOUNDS

Substance, symmetry and type	Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
<i>Methane and Ethane Derivatives</i>							
Methane CH_4	Cub.	(y), (bm)	T_d^2 (?)	4	T_d	5.89	1931, 307, 308, 309.
Iodoform CHI_3	Hex.	(z), (bn)	C_6^2	2	C_3	6.818	1931, 221.
Pentaerythritol Tetrabromide $\text{C}(\text{CH}_2\text{Br})_4$	Mon.	(bo)	C_{2h}^1	1	C_2^h	7.199	1932, 457.
Pentaerythritol Tetrachloride $\text{C}(\text{CH}_2\text{Cl})_4$	Mon.	(bo)	C_{2h}^1	1	C_2^h	6.912	1932, 457.
Pentaerythritol Tetraiodide $\text{C}(\text{CH}_2\text{I})_4$	Mon.	(bo)	C_{2h}^1	1	C_2^h	6.432	1932, 457.
Urea $\text{CO}(\text{NH}_2)_2$	Tet.	(aa), (bp)	V_d^2	2	C_2^2	6.432 $\beta = \text{ca } 113^\circ$	1932, 484; 1934, 303.
Thiourea $\text{CS}(\text{NH}_2)_2$	Ort.	(ab), (bq)	V_h^{16}	4	C_6	5.50	1932, 485.
Methyl Urea $\text{CONH}_2(\text{NHCH}_3)$	Ort.	(ac), (br)	V^4	4	C_2	6.89	1925, 281; 1933, 103.
Guanidinium Chloride $(\text{NH}_2)_2\text{CNH} \cdot \text{HCl}$	Ort.		V_h^{16}	8		7.76	1931, 444.
Hexabromobutylene $\text{CHBr}_2\text{BrC}=\text{CBr}_2\text{CHBr}_2$	Mon.		C_{2h}^6	2	C_i	11.5	1931, 104; 1932, 142.
Hexamethylethane $\text{C}_2(\text{CH}_3)_6$	Cub.			2		7.69	1934, 289.
Hexachlorethane (above 71°C) C_2Cl_6	Cub.			2		7.43 at 80°C	1934, 289.

Amino Acids

α -Glycine $\text{CH}_2\text{NH}_2\text{COOH}$	Mon. (bs)	C_{2h}^s	4	5.04	12.1 $\beta = 111^\circ 38'$	5.41	1931, 41, 173.
β -Glycine $\text{CH}_2\text{NH}_2\text{COOH}$	Mon. (bs)	C_2^s	2	5.18	6.18 $\beta = 114^\circ 20'$	5.29	1931, 41.
d-Alanine $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	Ort.	V^4	4	6.0	12.1	5.75	1931, 41.
dl-Alanine $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	Ort.	C_2^{2v}	4	6.0	12.0	5.8	1931, 41.
α -Glycylglycine $\text{CH}_2\text{NH}_2\text{CONHCH}_2\text{COOH}$	Mon. (bt)	C_2^s	4	7.76	9.46 $\beta = 99^\circ 30'$	7.67	1931, 41; 1932, 283.
β -Glycylglycine $\text{CH}_2\text{NH}_2\text{CONHCH}_2\text{COOH}$	Mon.	C_{2h}^s	4	17.3	4.65 $\beta = 125^\circ 20'$	8.4	1931, 41.
γ -Glycylglycine $\text{CH}_2\text{NH}_2\text{CONHCH}_2\text{COOH}$	Ort.	C_2^{2v}	4	8.1	9.36	7.7	1931, 41.
Asparagine Monohydrate $(\text{CONH}_2)\text{CHNH}_2\text{CH}_2\text{COOH} \cdot \text{H}_2\text{O}$	Ort.	V^4	4	5.6	11.8	9.86	1931, 41.
d-Alanyl-glycine $\text{NH}_2 \cdot \text{CH}(\text{CH}_3)\text{CONHCH}_2\text{COOH}$	Mon.		2	5.29	11.67 $\beta = 101^\circ 30'$	5.47	1932, 283.
α -Diglycylglycine $\text{NH}_2\text{CH}_2\text{CONHCH}_2\text{CONHCH}_2\text{COOH}$	Mon.		2	8.53	4.3 $\beta = 105^\circ 30'$	11.4	1932, 283.
β -Diglycylglycine $\text{NH}_2\text{CH}_2\text{CONHCH}_2\text{CONHCH}_2\text{COOH}$	Mon.		4	14.6	4.79 $\beta = 105^\circ 30'$	11.67	1932, 283.
Diglycylglycine Dihydrate $\text{NH}_2\text{CH}_2\text{CONHCH}_2\text{CONHCH}_2\text{COOH} \cdot 2\text{H}_2\text{O}$	Ort.	C_2^{2v}	4	22.0	9.8	4.7	1931, 41.
l-Aspartic Acid $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2)\text{COOH}$	Mon.	C_2^s	4	5.1	6.9 $\beta = 96^\circ$	15.1	1931, 41.
l-Glutamic Acid $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	Ort.	V^4	4	7.06	10.3	8.75	1931, 41.
l-Cystine $\text{COOHCH}(\text{NH}_2)\text{CH}_2\text{S} = \text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	Hex. (bu)						1931, 22, 41.

Substance, symmetry and type	Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
<i>Other Dicarboxylic Acid Derivatives</i>							
Oxalic Acid Dihydrate (COOH) ₂ · 2H ₂ O	C _{2h} ⁶	2	C ₁	6.12	3.61 $\beta = 106^\circ 12'$	12.03	1934, 305a.
α -Malonic Acid COOHCH ₂ COOH (form stable above 80° C)	Ort.	16		8.70	11.53	17.05	1931, 98; 1932, 131.
β -Succinic Acid COOH(CH ₂) ₂ COOH (room temp. form)	Mon.						1930, 383; 1931, 98; 1932, 131.
α -Succinic Acid COOH(CH ₂) ₂ COOH (second modification)	Mon.	8		5.70	26.28 $\beta = 115^\circ 45'$	7.57	1931, 98; 1932, 131.
α -Glutaric Acid COOH(CH ₂) ₃ COOH	C _{2h} ⁴	8		10.34	5.08 $\beta = 129^\circ 0'$	32.9	1932, 131, 132.
β -Glutaric Acid COOH(CH ₂) ₃ COOH	C _{2h} ⁶			10.06	4.87 $\beta = 132^\circ 35'$	17.4	1932, 131, 132.
Guanidine d-Tartrate Hydrate [C(NH ₂) ₂ NH] ₂ (C ₄ H ₆ O ₆) · 1½H ₂ O	Mon.	2		9.88	14.77 $\beta = 104^\circ 57'$	4.78	1933, 458.
<i>Long Chain Derivatives</i>							
Dodecanol C ₁₂ H ₂₆ OH	D _{2d} ¹	1	D ₂ ¹	4.76		34.0	1932, 41, 42.
Hexadecanol C ₁₆ H ₃₄ OH	C _{2h} ⁴	4		8.80	4.90 $\beta = 56^\circ 40'$	44.2	1932, 41.
α -Palmitic Acid CH ₃ (CH ₂) ₁₄ COOH	Mon.	4		9.41	5.00 $\beta = 50^\circ 33'$	46.1	1932, 131, 133, 441.
α -Stearic Acid CH ₃ (CH ₂) ₁₆ COOH	Mon.	4		9.41	5.00 $\beta = 50^\circ 50'$	45.9	1932, 131, 440.

β -Stearic Acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Mon.	(ao)	C_{17}^{h} or C_{16}^{h}	4	5.54	7.38 $\beta=63^\circ 38'$	48.84	1932, 131, 133, 440.
<i>Saturated Cyclohydrocarbons and their Derivatives</i>								
Cyclohexane	Cub.		T_6^{h} or O_6^{h}	4	C_6^{i}	8.41 at CO_2 -acetone temp.		1930, 122a.
C_6H_{12}								
1, 4 Dibromocyclohexane	Mon.	(bx)	C_6^{h}	2	C_i	11.92	6.02	1931, 161, 1932, 191.
$\text{C}_6\text{H}_{10}\text{Br}_2$								
1, 4 Diiodocyclohexane	Mon.	(bx)	C_6^{h}	2	C_i	12.50	6.20	1931, 161, 1932, 191.
$\text{C}_6\text{H}_{10}\text{I}_2$								
α -Cyclohexandiol 1, 2	Ort.		V_6^{h}	8		7.62	19.57	1931, 473.
$\text{C}_6\text{H}_{10}(\text{OH})_2$								
β -Cyclohexandiol 1, 4	Mon.		C_6^{h}	6		6.32	7.27	1931, 473; 1932, 192.
$\text{C}_6\text{H}_{10}(\text{OH})_2$								
γ -Cyclohexandiol 1, 2	Mon.		C_6^{h}	8		19.13	7.23	1931, 473.
$\text{C}_6\text{H}_{10}(\text{OH})_2$								
β -Cyclohexandiol Diacetate 1, 4	Mon.		C_6^{h}	2	C_i	13.56	6.72	1931, 473.
$\text{C}_6\text{H}_{10}(\text{CH}_3\text{CO}_2)_2$								
Quercitol	Mon.		C_2^{i}	2		6.83	6.45	1931, 471.
$\text{C}_6\text{H}_7(\text{OH})_5$								
l-Inositol	Mon.		C_2^{i}	2		6.17	6.83	1931, 471.
$\text{C}_6\text{H}_6(\text{OH})_6$								
i-Inositol	Mon.		C_6^{h}	8	A	6.64	19.7	1931, 471.
$\text{C}_6\text{H}_6(\text{OH})_6$								
i-Inositol Dihydrate	Mon.		C_6^{h}	4		8.98	6.49	1931, 472.
$\text{C}_6\text{H}_6(\text{OH})_6 \cdot 2\text{H}_2\text{O}$								
Methyl-l-Inositol	Mon.		C_2^{i}	2		6.60	8.65	1931, 350.
$\text{C}_6\text{H}_6(\text{OH})_6(\text{OCH}_3)$ (Quebrachitol)								
Cyclododecane	Tri.			1		7.84	7.82	1933, 307.
$\text{C}_{12}\text{H}_{24}$								

$\alpha=81^\circ 42'$, $\beta=64^\circ$, $\gamma=81^\circ$

β -Methyl-l-Arabinoside $C_6H_{12}O_6$	Ort. Form	V^4	4	16.56	7.74	5.89	1933, 108.
β -Methyl-l-Arabinoside $C_6H_{12}O_6$	Mon. Form	C_2^2 or C_2^{2h}	2	8.96	7.73 $\beta=115^\circ 54'$	5.94	1934, 27.
2, 3, 4 Trimethyl- δ -l-Arabinolactone Ort.		V^4	4	10.8	12.2	7.30	1931, 492.
α -Methylxyloside $C_6H_{12}O_6$	Mon.	C_2^2	4	11.28	6.72 $\beta=112^\circ 12'$	11.02	1932, 115, 1934, 27.
β -d-Methylxyloside $C_6H_{12}O_6$	Mon.	C_2^2	2	7.82	6.89 $\beta=113^\circ 10'$	7.74	1932, 113.
2, 3, 4 Trimethyl- α -d-Xylopyranose Mon.		C_2^2	2	8.68	8.31 $\beta=91^\circ 0'$	6.65	1931, 492.
β -d-Glucosan $C_6H_{10}O_6$	Ort.	V^4	4	6.65	13.14	7.46	1933, 108.
Methyl-l-Rhamnoside $C_7H_{14}O_6$	Ort.	V^4	4	8.26	13.31	7.54	1934, 27.
α -Methyl-d-Glucoside $C_7H_{14}O_6$	Ort. (ap)	V^4	4	11.21	14.57	5.29	1933, 108.
β -Methyl-d-Glucoside Hemihydrate $C_7H_{14}O_6 \cdot \frac{1}{2}H_2O$	Tet.	D_4^2	8	7.32		33.6	1933, 108.
1, 3, 4, 5 Tetramethyl- β -d-Fructopyranose Ort.		V^4	4	9.22	8.97	14.8	1931, 492.
1, 3, 4, 5 Tetraacetyl- β -d-Fructopyranose Mon.		C_1^2	2	10.7	7.98 $\beta=144^\circ 30'$	17.0	1931, 492.
α -Methylmannoside (m. p. 193° C) $C_7H_{14}O_6$ (pyranose form)	Ort.	V^4	4	9.38	9.99	9.23	1932, 118.
α -Methylmannoside (m. p. 118° C) $C_7H_{14}O_6$ (furanose form)	Ort.	V^4	4	15.87	11.73	4.64	1932, 118.
γ -d-Mannonolactone	Ort.		4	14.0	11.1	4.73	1931, 492.

<i>Substance, symmetry and type</i>	<i>Space group</i>	<i>No. mol. per cell</i>	<i>Min. mol. symmetry</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>References</i>
2, 3, 5, 6 Tetramethyl- γ -d-Mannonolactone Mon.	C_2^2	2		9.79	13.8 $\beta = 93^\circ 18'$	4.50	1931, 492.
γ -Monoacetylmethyl-L-Rhamnoside $C_8H_{16}O_6$ Ort.	V^4	4		7.98	18.25	7.08	1933, 108.
Glucose Pentaacetate Ort.		4		24.3	14.9	5.65	1934, 151.
2, 3, 5 Trimethyl- γ -L-Rhamnonolactone Ort.	V^1	4		12.2	18.3	4.65	1931, 492.
d-Chitosamine Hydrochloride $C_6H_{14}O_2NCl$ Mon. Cellulose ($C_6H_{10}O_5$) _n	C_2^2	2		7.68	9.18 $\beta = 112^\circ 29'$	7.11	1933, 108. 1930, 448; 1931, 21, 82, 491.
Cellulose Hydrate Mon. (<i>by</i>)				8.14	10.3 $\beta = 62^\circ$	9.14	1929, 46; 1933, 402.
Cellulose Perchlorate $2C_6H_{10}O_5 \cdot HClO_4$ Mon. (<i>by</i>)				16.5	10.3 $\beta = 93^\circ$	10.7	1930, 372.

(bn) A further study of the structure of iodoform, CHI_3 , using photographic data, has confirmed the previous choice of space group and iodine positions. Carbon atoms are thought to be in $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3}$, $\frac{1}{3}$, $u+\frac{1}{2}$ with u between 0.50 and 0.60.

(bo) If the space group assigned to these pentaerythritol tetrahalides is correct, their molecules cannot have tetrahedral symmetry.

(bp) Additional spectrometric measurements on urea and their Fourier analyses have led to the following more accurate parameters (see book, p. 373): $u(\text{C})=0.335$, $v(\text{O})=0.60$, $w(\text{N})=0.145$, $t(\text{N})=0.18$.

(bq) Spectrometric measurements of intensity and Fourier analyses have been used in a reexamination of the structure of thiourea, $\text{CS}(\text{NH}_2)_2$. Atoms are in the positions of V_h^{16} previously chosen, (ab), with the parameters (the origin in a center of symmetry):

C: (c) $\pm(uv\frac{1}{4})$; $\pm(\frac{1}{2}-u, v+\frac{1}{2}, \frac{1}{4})$ with $u=-0.14$, $v=0.10$

S: (c) $\pm(u_1v_1\frac{1}{4})$; etc. with $u_1=0.120$, $v_1=-0.007$

N: (d) $\pm(xyz)$; $\pm(x, y, \frac{1}{2}-z)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, \bar{z})$
with $x=0.278$, $y=-0.130$, $z=-0.125$.

The way the molecules pack together is illustrated by Figure 335. In contrast with the earlier arrangement all the atoms in a molecule lie in one plane. The C-S separation is 1.64 Å; NH_2 and S of different molecules are 3.45 Å apart. Other interatomic distances are practically the same as in urea.

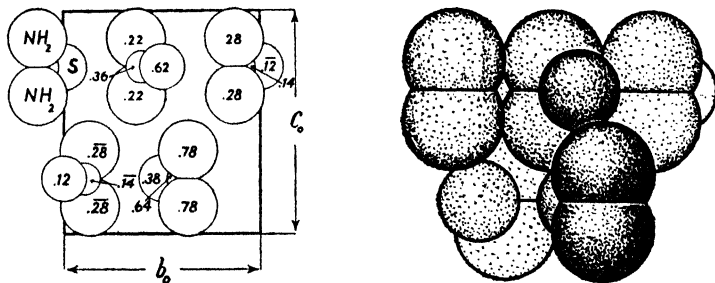


FIG. 335a.—(left) The orthorhombic structure of thiourea projected on the a -face.

FIG. 335b.—(right) A packing drawing of a . The C atoms do not appear.

(br) Spectrometric measurements of crystals of methyl urea, $\text{CONH}_2 \cdot (\text{NHCH}_3)$, have been made in an attempt to find its complete structure. All atoms are in general positions of V^4 . Values of x and y atomic parameters have been determined from structure factor calculations and Fourier analysis. They account for all the $(hk0)$ reflections but a satisfactory

structure using them in an explanation of the more complicated (h0l) data was not found.

(bs) A structure for the ordinary (α) form of **glycine**, $\text{CH}_2\text{NH}_2\text{COOH}$, has been deduced which is in good agreement with spectrometric measurements of the simplest reflections but which like that mentioned for methyl urea, (*br*), is unable to explain the more complex intensities. In this proposed arrangement all atoms are in general positions of C_{2h}^6 : (e) $\pm(xyz)$; $\pm(\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z)$ with the parameters of Table V.

It has been reported that X-ray results indicate the reality of the supposed β -modification of glycine but the published evidence for this conclusion is not convincing.

TABLE V. PARAMETERS OF THE ATOMS IN GLYCINE

Atom	No. per cell	x	y	z
O(1)	4	0.42	0.35	0.74
O(2)	4	.44	.47	.63
N	4	.88	.33	.15
C(1)	4	.22	.41	.58
C(2)	4	.12	.40	.26

(bt) By choosing axes in the ac-plane different from those of Table IV, α -**glycylglycine** has been given a four-molecule cell with the dimensions $a_o=7.7$, $b_o=9.56$, $c_o=9.5$, $\beta=125^\circ 20'$ (1931, 41).

(bu) Conflicting cell dimensions have been published for the hexagonal crystals of **l-cystine**. One determination (1931, 41), choosing D_6^2 as space group, finds a six-molecule cell with $a_o=5.40$ A, $c_o=57.8$ A. The other with three molecules in its unit has $a_o=9.40$ A, $c_o=9.42$ A (1931, 22).

(bv) Recent measurements of the unit cell of the room temperature form of **succinic acid** (1931, 98; 1932, 131) confirm a previous assignment of unit cell.

(bw) The simple hexagonal unit found for **dodecanol** at room temperature is considered to show that its molecules are rotating.

(bx) Positions have been found for the iodine atoms in **1,4 diiodocyclohexane**. They are in general positions of C_{2h}^6 : (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$ with $x=0.150$, $y=0.135$ or 0.365 , $z=0.385$. An earlier space group assignment, of C_{2h}^4 (1931, 161), was wrong for this compound and for the isomorphous dibromide.

(by) Debate over the unit cell and structure of cellulose continues, the symmetry being sometimes treated as tetragonal, sometimes as orthorhombic and sometimes as monoclinic. The last is most probably correct. It is obvious that from the standpoint of sound crystal analysis the arrangements frequently described for cellulose and its derivatives must be considered as speculations, more or less compatible with chemical information, and perhaps not conflicting with the very limited X-ray data at

hand. Assignments of positions to the atoms in rubber, in silk fibroin and in most other macromolecular substances are equally uncertain.

Aromatic Compounds

Greater progress has been made in determining atomic positions in crystals of aromatic compounds. This is largely due to the fact that their benzene rings provide large building blocks that always have the same size and shape and can enter into the known units in only a limited number of ways.

(bz) It has been found that the iodine atoms in *o*-iodobenzoic acid, C_6H_4ICOOH , are in general positions of C_{2h}^5 : (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$ with the parameters $x=0.14$, $y=0.08$, $z=0.02$. The positions of the other atoms are not known.

(ca) *p*-Dibromobenzene, $C_6H_4Br_2$, has its bromine atoms in general positions of C_{2h}^5 : (c) $\pm(xyz)$; $\pm(\bar{x}, y+\frac{1}{2}, \frac{1}{2}-z)$ with $x=0.03$, $y=0.167$, $z=0.170$. For the isomorphous chloride $x_1=0.04$, $y_1=0.16$, $z_1=0.16$. Parameters compatible with atomic packing and with observed optical properties have been suggested for the carbon atoms. The available X-ray data are not able to show whether these carbon positions are right.

The diffraction effects of *p*-bromochlorobenzene, C_6H_4BrCl , are intermediate between those of the chlorine and bromine derivatives. This presumably means that the molecules go into the structure, with half the bromine atoms pointing one way and with the other half pointing in the opposite direction.

(cb) The *p*-diiodobenzene, $C_6H_4I_2$, is not isomorphous with its chloro- and bromo-analogues. Iodine atoms in the orthorhombic unit are in general positions of V_h^{15} : (c) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, \bar{z})$; $\pm(\bar{x}, y+\frac{1}{2}, \frac{1}{2}-z)$; $\pm(\frac{1}{2}-x, \bar{y}, z+\frac{1}{2})$ with $x=0.172$, $y=0.40$, $z=0.22$.

m-Diiodobenzene also is orthorhombic. Iodine atoms are at $\pm(uv\frac{1}{4})$; $\pm(u\bar{v}\frac{3}{4})$; $\pm(u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{4})$; $\pm(\frac{1}{2}-u, v+\frac{1}{2}, \frac{1}{4})$ with $u=0.172$, $v=0.200$. The space group may be C_{2v}^{12} .

(cc) A thorough study, including spectrometric measurements and a Fourier analysis, has been made of the crystal structure of *drene*, 1, 2, 4, 5 $C_6H_2(CH_3)_4$. All atoms are in general positions of C_{2h}^5 : (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$ with the parameters listed in Table VII. This arrangement (Figure 336) gives a molecule that, like $C_6(CH_3)_6$, is planar. The packing is, however, a totally different one. In this crystal the nearest approach of atoms belonging to adjacent molecules is relatively large—3.90 Å.

(cd) The x and z parameters of both the chlorine and the carbon atoms in C_6Cl_6 have been selected from a Fourier analysis of the spectrometrically determined (h0l) intensities. Data needed to establish the y parameters could not be obtained so that the structure remains only partly known.

TABLE VI. THE CRYSTAL STRUCTURES OF AROMATIC ORGANIC COMPOUNDS

Substance, symmetry and type		Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
Benzene C_6H_6	Ort. (au)							1930, 45a; 1932, 117.
Phenylaminoacetic Acid $C_6H_5CHNH_2COOH$	Ort.							1931, 354.
d-Phenyl Alanine $C_6H_5CH_2 \cdot CH(NH_2)COOH$	Ort.	V^4	8	A	30.8	11.0	4.8	1931, 41.
o-Iodobenzoic Acid C_6H_4ICOOH	Mon. (bz)	C_{2h}^5	4		11.30	15.17	4.336	1933, 262.
p-Dibromobenzene $C_6H_4Br_2$	Mon. (ca)	C_{2h}^5	2	C_i	4.11	5.80	15.46	1932, 202.
p-Dichlorobenzene $C_6H_4Cl_2$	Mon. (ca)	C_{2h}^5	2	C_i	4.10	5.88	14.83	1932, 202.
p-Bromochlorobenzene C_6H_4BrCl	Mon. (ca)	C_{2h}^5	2	C_i	4.13	5.81	15.15	1932, 202.
o-Diiodobenzene $C_6H_4I_2$	Mon. (cb)	C_{2v}^{12}	4		8.29	12.23	7.91	1933, 181.
m-Diiodobenzene $C_6H_4I_2$	Ort. (cb)	C_{2v}^{12}	4	C_s	17.20	7.08	6.21	1933, 181.
p-Diiodobenzene $C_6H_4I_2$	Ort. (cb)	V_h^{16}	4	C_i	17.00	7.38	6.21	1933, 181.
p-Quinone $C_6H_4O_2$	Mon. (co)	C_{2h}^5	2	C_i	7.08	6.79	5.80	1932, 96; 1934, 228.
Resorcinol $m-C_6H_4(OH)_2$	Ort.	C_{2v}^9	4		10.53	9.53	5.66	1928, 451; 1934, 229a.
m-Dinitrobenzene $C_6H_4(NO_2)_2$	Ort. (aw)	V_h^{16}	4	C_s	13.27	14.06	3.820	1931, 171.

1, 2, 6 Dinitrophenol $C_6H_4OH(NO_2)_2$	Ort.	V_h^{11}	8	12.1	12.7	9.5	1930, 134.
2, 4, 6 Trinitrobenzene $C_6H_2Br(NO_2)_3$	Tri.		12*	15.2	15.4	15.64	1933, 185.
2, 4, 6 Trinitrobenzene $C_6H_2Br(NO_2)_3$	Hex.		9	14.90		22.6	1933, 185.
2, 4, 6 Trinitrochlorobenzene $C_6H_2Cl(NO_2)_3$	Mon.	C_{2h}^2	8	24.9	6.8	11.0	1933, 185.
Durene 1, 2, 4, 5 $C_6H_2(CH_3)_4$	Mon. (cc)	C_{2h}^5	2	11.57	5.77	7.03	1933, 377, 378.
2, 4, 6 Trinitroiodobenzene $C_6H_2I(NO_2)_3$	Tet.	D_{3h}^4	4	7.03		19.80	1933, 185.
1, 2, 4, 6 Tetrannitrobenzene $C_6H_2(NO_2)_4$	Ort.	V^4	4	12.4	6.15	13.1	1933, 185.
2, 4, 6 Trinitrotoluene $C_6H_2CH_3(NO_2)_3$	Mon. (ck)	C_{2h}^6		40.5	6.19	15.2	1933, 186.
2, 4, 6 Trinitroaniline $C_6H_2(NH_2)(NO_2)_3$	Mon.	C_{2h}^5	4	15.3	9.28	6.01	1933, 185.
4 Nitro-2-Methylaminotoluene (yellow form)	Mon.	C_{2h}^5	4	17.2	12.2	3.83	1932, 211.
4 Nitro-2-Methylaminotoluene (red form)	Tri.		2	7.6	8.5	7.5	1932, 211.
Styphnic Acid $C_6H(OH)_2(NO_2)_3$	Hex. (cl)	C_{2v}^2 or D_{3d}^4	6	12.7		10.0	1931, 190.
Hexachlorobenzene C_6Cl_6	Mon. (cd)	C_{2h}^6	2	8.07	3.84	16.61	1931, 283.
Hexaminobenzene $C_6(NH_2)_6$	Cub.	O_h^2	16	14.84	at $-183^\circ C$		1931, 261.

* A triclinic unit containing as many molecules as 12 cannot possibly be the true one.

Substance, symmetry and type		Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
2, 4, 6 Trinitrophenol	Hex. (cl)	C_{3v}^2 or D_{3d}^5	6		13.4		9.6	1931, 190.
Quinhydrone	Mon. (ce)	C_{2h}^5	1		3.85	6.04	10.9	1932, 150.
$C_6H_4O_2 \cdot C_6H_4(OH)_2$						$\beta = 90^\circ$		
p-Aminoazobenzene	Mon.		4		13.69	5.604	14.18	1933, 365.
$C_6H_5N = NC_6H_4(NH_2)$						$\beta = 81^\circ 49'$		
o-Azotoluene	Mon.	C_{2h}^5	4		13.93	6.604	14.55	1932, 358.
$(CH_3)C_6H_4N = NC_6H_4(CH_3)$						$\beta = 79^\circ 9'$		
2, 4, 6 Trinitrophenylamine	Mon.	C_{2h}^5	8	A	22.0	7.8	16.2	1931, 189.
$C_6H_6(NH)C_6H_3(NO_2)_3$						$\beta = 107^\circ$		
Aniline Picrate	Mon.	C_{2h}^5	4		13.2	7.4	15.2	1931, 189.
$C_6H_5NH_2 \cdot \dots (OH)C_6H_3(NO_2)_3$						$\beta = 93^\circ$		
Ethyl Anisal p-Amino Cinnamate	Mon.	C_{2h}^5	4		6.65	7.88	45.6	1933, 40a.
$C_{14}H_{16}NO_5$						$\beta = 135^\circ 35'$		
p-Azoxyanisole*	Mon.	C_{2h}^5	4		11.0	8.10	14.95	1933, 40a; 1934, 302.
$C_{14}H_{14}N_2O_3$						$\beta = 107^\circ 30'$		
p-Azoxyphenetole	Mon.	C_4^2	4		15.4	5.41	17.6	1933, 40a.
$C_{16}H_{18}N_2O_3$						$\beta = 94^\circ$		
Dibenzylidenebenzidine	Mon.	C_{2h}^5	2	C_i	5.9	7.7	1933, 40a.	
						$c \sin \beta = 21.5 \text{ \AA}$		
Dibenzyl	Mon. (cm)	C_{2h}^5	2	C_i	12.77	6.12	7.70	1934, 70, 227, 229.
$C_6H_5CH_2 - CH_2C_6H_5$						$\beta = 116^\circ$		
Stilbene	Mon. (cm)	C_{2h}^5	4		12.20	5.72	16.00	1933, 364.
$C_6H_5CH = CHC_6H_5$						$\beta = 113^\circ 48'$		

Tolane	Mon.	(<i>cm</i>)	4	12.80	5.68	15.74	1933, 364.
$C_6H_5C \equiv CC_6H_5$					$\beta = 114^\circ 56'$		
p-Nitrostilbene	Ort.		8	7.94	28.3	10.22	1931, 188.
$C_6H_5CH = CHC_6H_4(NO_2)$							
p-Cyano-o-Nitro-p'-Methoxystilbene	V_h^9, V_h^6 or C_{2v}^{11}		8	14.2	27.8	7.6	1932, 212.
$C_6H_5(CN)(NO_2)CH = CHC_6H_4(OCH_3)$ (metastable yellow form)	Ort.						
p-Cyano-o-Nitro-p'-Methoxystilbene			2	8.50	7.45	13.35	1932, 212.
$C_6H_5(CN)(NO_2)CH = CHC_6H_4(OCH_3)$ (orange form)	Tri.				$\alpha = 98^\circ 6', \beta = 106^\circ 20', \gamma = 75^\circ 40'$		
Stilbene+2 mol. 1, 3, 5 Trinitrobenzene			2	12.7	15.4	7.7	1931, 192.
$C_6H_5CH = CHC_6H_3 \cdot 2[C_6H_3(NO_2)_3]$	Tri.				$\alpha = 102^\circ 16', \beta = 85^\circ 30', \gamma = 87^\circ 35'$		
Diphenylbutadiene	Mon.		4	7.71	11.70	13.41	1930, 401.
$C_6H_5CH = (CH)_2 = CHC_6H_5$					$\beta = 97^\circ$		
Diphenylhexatriene	Mon.		2	6.63	7.43	14.43	1930, 401.
$C_6H_5CH = (CH - CH)_2 = CHC_6H_5$					$\beta = 90^\circ$		
Diphenyloctatetraene	Mon.		2	6.25	7.44	16.03	1930, 401.
$C_6H_5(CH = CH)_4C_6H_5$					$\beta = 90^\circ$		
Diphenyldecapentaene	Ort.		4	10.25	7.66	21.2	1930, 401.
$C_6H_5(CH = CH)_5C_6H_5$							
Diphenyldodecahexaene	Ort.		4	10.20	7.60	23.58	1930, 401.
$C_6H_5(CH = CH)_6C_6H_5$							
Diphenyltetradecaheptaene	Ort.		4	10.2	7.57	25.95	1930, 401.
$C_6H_5(CH = CH)_7C_6H_5$							
Diphenyl Disulfide (C_6H_5S) ₂	Ort.		4	23.5	8.21	5.63	1932, 137, 188.
Diphenyl Diselenide (C_6H_5Se) ₂	Ort.		4	23.70	8.25	5.64	1932, 137, 188.

* In 1934, $a_o = 16.0$ A, $b_o = 8.08$ A, $c_o = 20.5$ A, $\beta = 107^\circ 30'$, C_{2h}^4 , 8 mol.

<i>Substance, symmetry and type</i>	<i>Space group</i>	<i>No. mol. per cell</i>	<i>Min. mol. symmetry</i>	<i>a₀</i>	<i>b₀</i>	<i>c₀</i>	<i>References</i>
Dibenzyl Disulfide (C ₆ H ₅ CH ₂ S) ₂	Mon. C _{2h} ⁶ or C ₄ ¹	4		13.46	8.23 β = 99°30'	11.29	1932, 137.
Dibenzyl Diselenide (C ₆ H ₅ CH ₂ Se) ₂	Mon. C _{2h} ⁶ or C ₄ ¹	4		13.50	8.17 β = 99°30'	11.57	1932, 137.
Dibenzoyl Disulfide (C ₆ H ₅ CO S) ₂	Mon. C _{2h} ⁶	4		12.26	12.00 β = 107°40'	9.04	1932, 137.
Diphenyl Nitrosoamine C ₆ H ₅ N—NO—C ₆ H ₅	Mon. C _{2h} ³	16	A	17.08	8.867 ₆ β = 90°58'	28.07	1933, 366.
Diphenyl C ₆ H ₅ ·C ₆ H ₅	Mon. (<i>aw</i>), (<i>cg</i>)						
Diphenic Acid (COOH C ₆ H ₄) ₂	Ort. V _h ¹³	8		13.80	11.90	14.12	1931, 84, 354; 1932, 129; 1933, 359. 1931, 84.
Hexachlorodiphenyl (C ₆ H ₂ Cl ₆) ₂	Ort. * (?) V _h ¹⁶	8		15.80	8.54	21.48	1931, 84.
<i>o</i> -Tolidine (C ₆ H ₄ CH ₂ NH ₂) ₂	Ort.						1931, 84.
Naphthalene C ₁₀ H ₈	Mon. (<i>bb</i>), (<i>cg</i>)	2	C _i	8.29	5.97 β = 122°42'	8.68	1933, 379.
1 Brom-2-Naphthylamine C ₁₀ H ₇ Br(NH ₂)	Ort.	4		12.8	15.9	4.2	1931, 191.
4 Brom-1-Naphthylamine C ₁₀ H ₇ Br(NH ₂)	Ort.	8		25.2	16	4.2	1931, 191.
4 Brom-1-Naphthylamine, 2, 6 Dinitrophenol (red form) C ₁₀ H ₇ Br(NH ₂), C ₆ H ₃ OH(NO ₂) ₂	Mon. C _{2h} ⁶	4		9.5	13.5 β = 105°	13.8	1931, 191.

4 Brom-1-Naphthylamine, 2, 6 Dinitrophenol (yellow form)	4	14.0	8.0 $\beta = 102^{\circ}6'$	14.5	1931, 191.
$C_{10}H_4Br(NH_2)$, $C_6H_3OH(NO_2)_2$ Mon.					
1, 2 Naphthoquinone	2	3.84	8.10 $\beta = 118^{\circ}40'$	13.40	1932, 96.
$C_{10}H_6O_2$ Mon.					
1, 4 Naphthoquinone	4	13.50	7.74 $\beta = 121^{\circ}10'$	8.25	1932, 96.
$C_{10}H_6O_2$ Mon.					
Naphthazarin (Alizarin Black)	2	3.85	8.02 $\beta = 97^{\circ}6'$	14.5	1934, 201.
$C_{10}H_6O_2$ Mon.					
Acenaphthene, Styphnic Acid	2	9.05	14.8 $\beta = 99^{\circ}$	6.8	1932, 412.
$C_{10}H_6(CH_2)_2$, $C_8H(OH)_2(NO_2)_3$ Mon.					
Anisal 1, 5 Diaminonaphthalene	4	21.7	12.7 $\beta = 119^{\circ}30'$	7.7	1933, 40a.
$C_{12}H_{12}O_2N_2$ Mon.					
<hr/>					
Anthracene	2	8.58	6.02 $\beta = 125^{\circ}$	11.18	1933, 375, 376, 380.
$C_{14}H_{10}$ Mon.					
(<i>bb</i>), (<i>ch</i>)					
Anthraquinone	8	19.7	24.5	3.95	1930, 405.
$C_{14}H_8O_2$ Ort.					
1, 2 Anthraquinone	4	11.41	11.56 $\beta = 130^{\circ}30'$	9.30	1932, 96.
$C_{14}H_8O_2$ Mon.					
1, 4 Anthraquinone (tabular form)	2	4.19	5.81 $\beta = 101^{\circ}30'$	19.62	1932, 96.
$C_{14}H_8O_2$ Mon.					
1, 4 Anthraquinone (acicular form)	4	13.82	9.54 $\beta = 100^{\circ}50'$	7.31	1932, 96.
$C_{14}H_8O_2$ Mon.					
2, 7 Dinitroanthraquinone	4	5.7		38.4	1930, 405.
$C_{14}H_6(NO_2)_2O_2$ Tet.					
2, 7 Dinitroanthraquinone Fluorene	2	8.2	7.4	19.0	1930, 405.
$C_{14}H_6(NO_2)_2O_2$, $(C_6H_4)_2CH_2$ Tri.			$\alpha = 78^{\circ}$, $\beta = 82^{\circ}$, $\gamma = ca 80^{\circ}$		

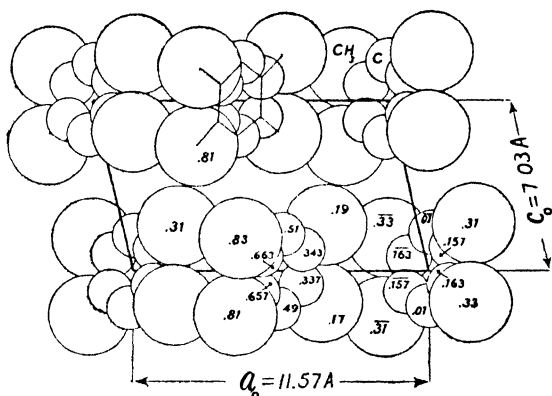
* Optical examination makes this crystal monoclinic.

Substance, symmetry and type		Space group	No. mol. per cell	Min. mol. symmetry	a_o	b_o	c_o	References
Mesanthraquinone	Ort.	V_6^6	8		19.65	24.57	4.00	1932, 96.
p-Diphenylbenzene (Terphenyl)	(ci)	C_{2h}^5	2	C_i	8.08	5.60	13.59	1933, 292, 359, 360.
$C_6H_4(C_6H_4)_2C_6H_6$	Mon.					$\beta=91^\circ55'$		
Chrysene	(cj)	C_{2h}^6 or C_4^4	4		8.34	6.18	25.0	1933, 214; 1934, 117.
$C_{18}H_{12}$	Mon.					$\beta=115^\circ48'$		
Quaterphenyl	(ci)	C_{2h}^3	2	C_i	8.14	5.64	18.4	1933, 187, 359.
$C_6H_4(C_6H_4)_2C_6H_4$	Mon.					$\beta=97^\circ$		
Triphenylbenzene	(cn)	C_{2v}^9	4		7.55	19.76	11.22	1933, 187; 1934, 157, 194.
$C_6H_3(C_6H_5)_3$	Ort.							
1, 2, 5, 6 Dibenzanthracene	Mon.	C_{2h}^2 or C_2^2	2		6.59	7.84	14.17	1933, 214.
Dianthracene	Ort.	V_6^6	4	C_i	8.18	12.15	18.75	1932, 207.
$(C_{14}H_{10})_2$	Ort.					$\beta=103^\circ30'$		
γ, γ' -Dibenzococcarbazole	Mon.		4		14.05	12.02	8.40	1931, 113.
Dimesityl	Mon.	C_{2h}^5	4		8.21	8.58	22.25	1930, 59; 1931, 84.
3, 3'-Diaminodimesityl	Mon.	C_{2h}^5	4		8.26	8.58	22.62	1930, 59; 1931, 84.
						$\beta=90^\circ$		

TABLE VII. PARAMETERS OF THE CARBON ATOMS IN DURENE

Atom	No. per cell	x	y	z
C(1)	4	0.188	0.314	0.267
C(2)	4	.093	.157	.127
C(3)	4	.037	-.005	.212
C(4)	4	-.055	-.162	.090
C(5)	4	-.108	-.325	.194

FIG. 336.—A projection upon the b-face of molecules in the monoclinic structure of durene, $C_6H_2(CH_3)_4$. The sizes given C and CH_3 in this drawing are without real significance.



All atoms are in general positions of C_{2h}^5 (not C_{2h}^4 , as previously chosen): (e) $\pm(xyz)$; $\pm(x, \frac{1}{2}-y, z+\frac{1}{2})$. The x and z parameters are given in Table VIII.

TABLE VIII. PARAMETERS OF THE ATOMS IN C_6Cl_6

Atom	x	z	Atom	x	z
C(1)	0.181	0.026	Cl(1)	0.412	0.070
C(2)	.118	.087	Cl(2)	.278	.205
C(3)	.048	-.062	Cl(3)	.133	-.137

(ce) A structure has been proposed for **quinhydrone**, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, which makes the oxygen atoms and hydroxyl groups equivalent. Though parameters have been published adequate data in support of them are lacking.

(cf) A partially described and tested structure has been suggested for **diphenyl**, $C_6H_5 \cdot C_6H_5$. No atomic coordinates have been published. The orientation of its molecule within the unit may be reproduced by rotating a planar $(C_6H_5)_2$ molecule having its center at a center of symmetry and its plane in bc. This rotation amounts to 32° about the c-axis and 20° about the b-axis.

(cg) A complete determination based upon quantitative intensity data and their Fourier analysis has been made of the atomic arrangement in **naphthalene**, $C_{10}H_8$. All atoms are in general positions of C_{2h}^5 : (e) $\pm(xyz)$;

$\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$ with the parameters of Table IX. The molecules of this grouping pack together as shown in Figure 337. Atoms of neighboring molecules come within 3.60 Å of one another.

TABLE IX. PARAMETERS OF THE ATOMS
IN NAPHTHALENE

Atom	x	y	z
C(1)	0.087	0.014	0.328
C(2)	.114	.162	.217
C(3)	.047	.104	.035
C(4)	.074	.251	-.078
C(5)	.007	.193	-.260

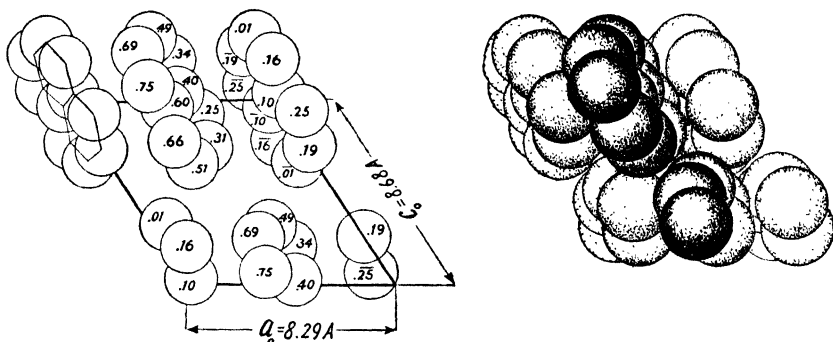


FIG. 337a.—(left) A projection of a portion of the monoclinic structure of naphthalene, $C_{10}H_8$, upon its b -face. The circles represent C atoms. Only parts of the molecules belonging to the bottom half of the cell are shown.

FIG. 337b.—(right) A packing drawing of a indicating the way the naphthalene molecules contact with one another.

(*ch*) The structure of **anthracene**, $C_{14}H_{10}$, also has been completely worked out from a series of spectrometer measurements and their Fourier analysis. Like naphthalene the atoms of its two-molecule monoclinic cell are in general positions of C_{2h}^b : (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$. The parameters are those of Table X. The close similarity that exists between this anthracene arrangement (Figure 338) and the naphthalene grouping (Figure 337) may be most easily seen by comparing the two figures. In anthracene contacting molecules are slightly farther apart, the nearest intermolecular atomic separation being 3.77–3.80 Å.

(*ci*) Another ring structure, established from quantitative data, is that of **p-diphenylbenzene**, $C_6H_5(C_6H_4)C_6H_5$. With its atoms also in general positions of C_{2h}^b : (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)$ (parameters in Table XI) this arrangement (Figure 339) is very similar to the two preceding. It

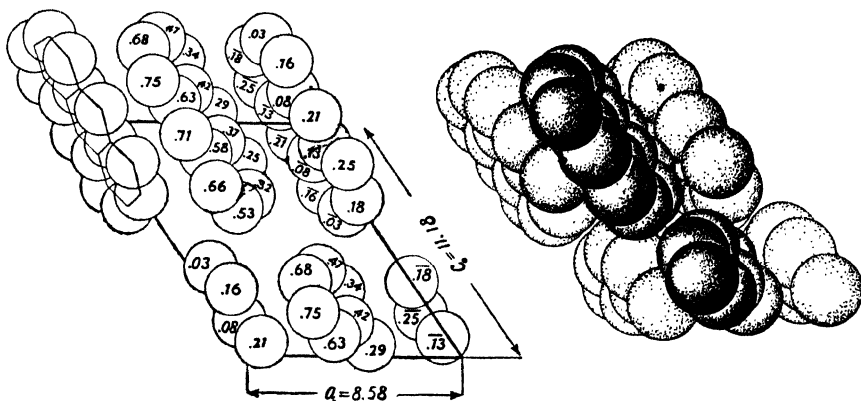


FIG. 338a.—(left) A portion of the monoclinic structure of anthracene, $C_{14}H_{10}$, projected on a b -face of its monoclinic unit. The close similarity between the arrangements found for naphthalene and anthracene may be seen by comparing Figures 337 and 338.

FIG. 338b.—(right) A packing drawing of a . In this and Figure 337b the radius chosen for the atomic spheres is that suggested by the closest approach of C atoms in adjacent molecules.

TABLE X. PARAMETERS OF THE ATOMS IN ANTHRACENE

Atom	x	y	z	Atom	x	y	z
C(1)	0.094	0.032	0.369	C(5)	0.033	0.130	-0.089
C(2)	.124	.157	.279	C(6)	.065	.254	-.179
C(3)	.062	.082	.140	C(7)	.002	.177	-.319
C(4)	.095	.207	.050				

TABLE XI. PARAMETERS OF THE ATOMS IN *p*-DIPHENYLBENZENE

Atom	x	y	z	Atom	x	y	z
C(1)	0.059	0.182	0.064	C(6)	-0.082	0.182	0.368
C(2)	-.046	0	.100	C(7)	-.187	0	.402
C(3)	-.105	-.182	.036	C(8)	-.246	-.182	.339
C(4)	-.094	0	.204	C(9)	-.200	-.182	.239
C(5)	-.036	.182	.268				

differs from them mainly in the fact that the long axes of its molecules are parallel to the ac -plane, whereas those of $C_{10}H_8$ and $C_{14}H_{10}$ are tilted at considerable angles.

Diphenyl, $C_6H_5 \cdot C_6H_5$, *p*-diphenylbenzene, $C_6H_5(C_6H_4)C_6H_5$, and quaterphenyl, $C_6H_5(C_6H_4)_2C_6H_5$, have nearly equal a_0 and b_0 axes and β angles. The molecules must therefore be similarly oriented in their crystals.

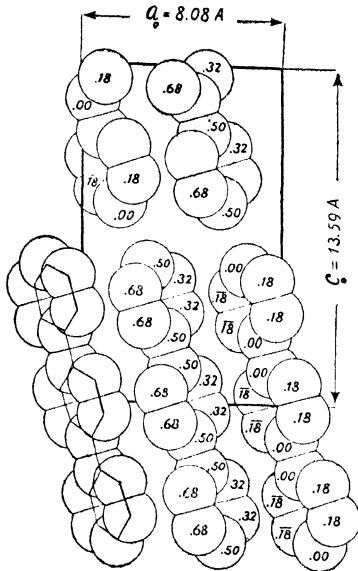


FIG. 339.—(left) A portion of the structure of *p*-diphenylbenzene, $C_6H_4(C_6H_5)_2$, projected on the *b*-face of its monoclinic unit. As in the figures immediately preceding circles represent C atoms. Only parts of the molecules associated with the upper half of the unit are included.

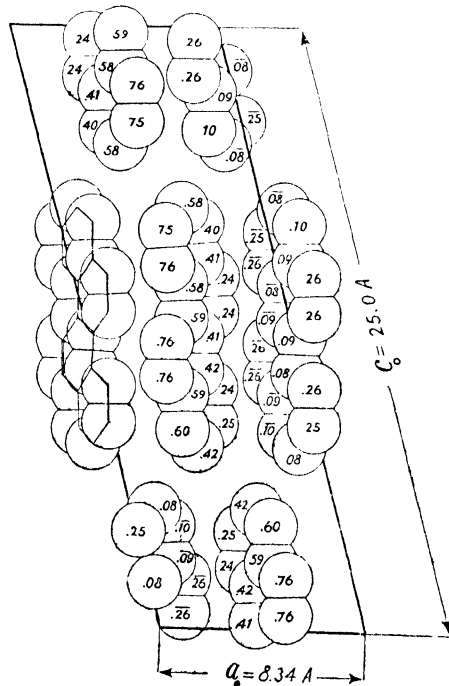


FIG. 340.—(right) A portion of the chrysene, $C_{18}H_{14}$, structure projected on its *b*-face. Only the molecules midway along the *c*-axis are fully shown.

TABLE XII. PARAMETERS OF THE ATOMS IN CHRYSENE

Atom	No. per cell	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	8	−0.026	0.086	0.013
C(2)	8	.018	.084	.074
C(3)	8	−.036	.256	.100
C(4)	8	.010	.254	.161
C(5)	8	.108	.079	.196
C(6)	8	.161	−.095	.171
C(7)	8	.116	−.089	.110
C(8)	8	.170	−.262	.084
C(9)	8	.125	−.260	.023

(cj) **Chrysene**, $\begin{array}{c} \text{C}_{10}\text{H}_6-\text{CH} \\ | \qquad \qquad \qquad || \\ \text{C}_6\text{H}_4-\text{CH} \end{array}$, differs from the preceding aromatic hydro-

carbons in having a four-molecule arrangement developed from C_{2h}^6 . All atoms are in the general positions: (f) $\pm(xyz)$; $\pm(\bar{x}, y, \frac{1}{2}-z)$; $\pm(x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2})$; $\pm(\frac{1}{2}-x, y+\frac{1}{2}, \bar{z})$. The parameters of Table XII, deduced from spectrometric measurements of intensity, lead to the symmetrical ring formula outlined in one of the molecules of Figure 340. Atoms of adjacent chrysene molecules come especially close to one another (ca 3.5 Å).

(ck) It is said that there exists a 1:1 compound of 2, 4, 6 $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$ and 2, 4, 6 $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$ which has cell dimensions identical with those of 2, 4, 6 $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$.

(cl) It is interesting that styphnic acid, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{OH})_2$, and 2, 4, 6 trinitrophenol, $\text{C}_6\text{H}_2(\text{NO}_2)_3(\text{OH})_3$, which differ by an OH group, should have similar crystal structures.

(cm) It has been pointed out (1933, 364) that azobenzene, $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$, stilbene, $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$, and tolane, $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ have cells of nearly the same shape and size.

The unit of dibenzyl, $\text{C}_6\text{H}_5\text{CH}_2-\text{CH}_2\text{C}_6\text{H}_5$, differs only in having a c-axis reported to be half as long. Two structures have been proposed for this crystal. One of them gives a molecule that is almost planar. The molecule of the other has its two phenyl groups stepped with respect to one another but lying in parallel planes. Unfortunately the atomic parameters for the second arrangement have not been given.

(cn) From a preliminary study of 1, 3, 5 triphenylbenzene, $\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)_3$, it has been concluded that the molecular centers are in general positions of C_{2v}^9 : (a) xyz ; $\bar{x}, \bar{y}, z+\frac{1}{2}$; $x+\frac{1}{2}, \frac{1}{2}-y, z$; $\frac{1}{2}-x, y+\frac{1}{2}, z+\frac{1}{2}$ with $z=0$. Atomic parameters have not yet been found.

(co) A preliminary note, without a complete description of atomic positions, has recently been published on **p-quinone**, $\text{C}_6\text{H}_4\text{O}_2$.

Recent Aliphatic Structures

(cp) Laue and spectral photographs have been used to assign positions to the atoms in **oxalic acid dihydrate**, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. The space group is C_{2h}^6 with two molecules per cell. Writing the coordinates of the general positions of this space group as (e) $\pm(xyz)$; $\pm(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$, the chosen atomic parameters are those of Table XIII. As can be seen from Figure 341, each water molecule is nearly equally distant (2.60–2.87 Å) from three oxygen atoms. Within a molecule C-C=1.59 Å, C-O=1.25 Å; the angle between C-O bonds is 126°.

TABLE XIII. PARAMETERS OF THE ATOMS IN
(COOH)₂·2H₂O

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.041	0.041	0.056
O(1)	.089	-.062	.150
O(2)	-.222	.222	.041
H ₂ O	-.444	-.375	.174

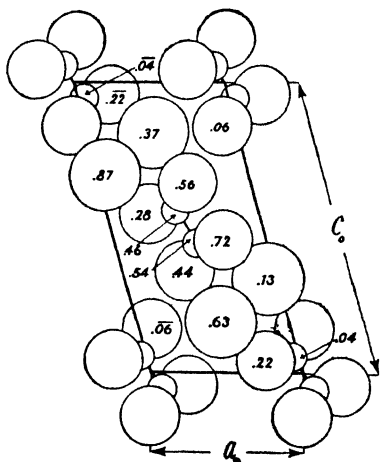



FIG. 341.—A b-face projection of the molecules of H₂C₂O₄·2H₂O associated with its monoclinic unit. The large circles are H₂O molecules. The O and OH of carboxyl groups, which are equivalent in this structure, are shown by the intermediate circles. The radii used in this figure were determined by convenience only.

(*cq*) A spectrometric study of hexamethylenetetramine, C₆H₁₂N₄, and a Fourier analysis of the intensities thus obtained are in complete agreement with one of the earlier investigations of this crystal. Carbon atoms are in (12a) *v*00; etc. [(*as*), book, p. 389], nitrogen in (8a) *uuu*; etc. with the same parameters: *u*=0.12, *v*=0.23.*

* On p. 390 of the book, values of *u* and *v* have been erroneously interchanged.

TABLE XIV. THE CRYSTAL STRUCTURES OF MISCELLANEOUS ORGANIC COMPOUNDS

Substance, symmetry and type	Space group	No. mol. per cell	Min. mol. symmetry	a_0	b_0	c_0	References
β -Polyoxymethylene	C_2^2 or C_3^2			4.46		17.35	1927, 126; 1932, 397, 406.
Eur-Polyethylene Oxide (CH_2CH_2O) _x (mol. wt. = ca 100,000)	C_2^4	36 (=x)		9.5	19.5 $\beta = 101^\circ$	12.0	1933, 405.
Hexuronic Acid $C_6H_8O_6$	C_2^2	4	A	17.71	6.32 $\beta = 102^\circ 30'$	6.38	1932, 116.
Diketopiperazine	C_2^6	2	C_i	5.19	11.5 $\beta = 83^\circ$	3.96	1931, 41.
							
$C_4H_8N_2O_2$							
$ON = CHCH = CN(NO)N = CO$				7.38	4.92 $\beta = 105^\circ 34'$	17.45	1931, 113.
Cyanuric Triazide $C_3N_3(N_3)_3$		2		8.66		5.94	1933, 457; 1934, 28.
Methylbixin $C_8H_{12}O_4$	C_2^6	4		10.56	13.40 $\beta = 121^\circ$	20.62	1930, 402; 1932, 458.
Choleic Acid*				25.9	13.69	7.20	1931, 199.
Thiophene C_4H_4S							
Monomeric Butadiene Sulfone $C_4H_4SO_2$	C_2^6	4		9.55	11.35 $\beta = 48^\circ 46'$	6.23	1930, 45a. 1932, 398.
Monomeric Isoprene Sulfone $C_4H_6SO_2$	C_2^4	2		6.60	7.62 $\beta = 69^\circ 26'$	6.67	1932, 398.

* If the formula of choleic acid is written as $8 C_4H_6O_4 + 1$ mol. palmitic or stearic acid (cf. Wieland and Sorge), this cell contains only half a molecule.

<i>Substance, symmetry and type</i>	<i>Space group</i>	<i>No. mol. per cell</i>	<i>Min. mol. symmetry</i>	<i>a₀</i>	<i>b₀</i>	<i>c₀</i>	<i>References</i>
Monomeric Dimethyl Butadiene Sulfone C ₄ H ₁₀ SO ₂ Ort.	V _h ¹⁶	4	C _s	7.55	12.12	7.39	1932, 398.
4 Isoxazolyl-5-Isoxazolyl Ketone C ₇ H ₄ N ₂ O ₄ Mon.		16	A	15.31	14.75 β=91°37'	12.77	1931, 113.
3, 4 Bis (5 Methyl-3-Isoxazolylcarbonyl) Furazan-2-Oxide C ₁₂ H ₈ N ₄ O ₆ Ort.		4		12.98	11.00	9.57	1931, 113.
5, 5 Diethyl Barbituric Acid (Veronal) C ₈ H ₁₂ N ₂ O ₃ Ort.	V _h ¹⁷	4	C ₂ ^v	7.11	14.4	9.7	1930, 404.
Veramon (Pyramidon, Veronal 1:1) Pyramidon Tri.	C _{2v} ⁸ or C _{2v} ⁴	4		27.1	12.2	7.20	1931, 187.
l-Ephedrine Hydrobromide C ₁₀ H ₁₅ ON, HBr Mon.	C ₂ ²	2		7.4	18.1	10.8	1931, 187.
l-Ephedrine Hydrochloride C ₁₀ H ₁₅ ON, HCl Mon.	C ₂ ²	2		12.74	6.20	7.62	1933, 155.
l-Ephedrine Hydroiodide C ₁₀ H ₁₅ ON, HI Ort.	V ₃	12	A	12.64	6.15	7.34	1933, 155.
Racemic Ephedrine Hydrobromide C ₁₀ H ₁₅ ON, HBr Mon.	C _{2h} ⁶	4		25.66	7.33	19.14	1933, 155.
Racemic Ephedrine Hydrochloride C ₁₀ H ₁₅ ON, HCl Mon.	C _{2h} ⁶	4		13.15	7.11	14.00	1933, 154.
Racemic Ephedrine Hydroiodide C ₁₀ H ₁₅ ON, HI Mon.	C _{2h} ⁶	4		13.27	7.04	13.44	1933, 154.
d-Pseudoephedrine Hydrobromide C ₁₀ H ₁₅ ON, HBr Ort.	V ₄	4		13.40	7.23	14.70	1933, 154.
				24.68	6.93	6.78	1933, 155.

d-Pseudoephedrine Hydrochloride $C_{10}H_{15}ON, HCl$ Ort.	V ⁴	4	25.49	6.48	6.91	1933, 155.
d-Pseudoephedrine Hydroiodide $C_{10}H_{15}ON, HI$ Ort.	V ⁴	4	11.39	6.83	15.62	1933, 155.
Racemic Pseudoephedrine Hydrobromide $C_{10}H_{15}ON, HBr$ Mon.	C ⁵ _{2h}	4	13.87	6.80	14.04	1933, 154.
Racemic Pseudoephedrine Hydrochloride $C_{10}H_{15}ON, HCl$ Ort.	V ¹⁸ _h	16	24.48	9.97	18.58	1933, 154.
Racemic Pseudoephedrine Hydroiodide $C_{10}H_{15}ON, HI$ Mon.	C ⁵ _{2h}	4	13.49	6.97	14.62	1933, 154.
d-Pseudococaine-l-Ephedrine-d-Tartrate Monohydrate $C_{21}H_{26}O_{11}N_2 \cdot H_2O$ Mon.		2	18.90	9.92	9.35	1932, 82.
d-Pseudococaine-l-Methyl Ephedrine-d-Tartrate Dihydrate $C_{22}H_{24}O_{11}N_2 \cdot 2H_2O$ Mon.		2	19.62	9.76	9.61	1932, 82.
l-Methyl Ephedrine Hydrobromide $C_{11}H_{17}ON, HBr$ Ort.	V ⁴	4	17.30	7.36	9.64	1934, 330.
l-Methyl Ephedrine Hydrochloride $C_{11}H_{17}ON, HCl$ Ort.	V ⁴	4	16.90	7.22	9.66	1934, 330.
l-Methyl Ephedrine Hydroiodide $C_{11}H_{17}ON, HI$ Ort.	V ³	8	6.10	31.60	13.25	1934, 330.
Racemic Methyl Ephedrine Hydrobromide (1st mod.) $C_{11}H_{17}ON, HBr$ Mon.	C ⁵ _{2h}	4	17.28	7.30	10.16	1934, 330.
Racemic Methyl Ephedrine Hydrobromide (2nd mod.) $C_{11}H_{17}ON, HBr$ Mon.	C ⁵ _{2h}	4	5.83	30.78	7.02	1934, 330.
Racemic Methyl Ephedrine Hydrochloride $C_{11}H_{17}ON, HCl$ Mon.	C ⁵ _{2h}	4	17.15	7.08	10.01	1934, 330.
Racemic Methyl Ephedrine Hydroiodide $C_{11}H_{17}ON, HI$ Tri.		2	11.2	7.67	7.68	1934, 330.
			$\alpha = 108^\circ 55', \beta = 95^\circ 36', \gamma = 84^\circ 15'$			

<i>Substance, symmetry and type</i>	<i>Space group</i>	<i>No. mol. per cell</i>	<i>Min. mol. symmetry</i>	<i>a₀</i>	<i>b₀</i>	<i>c₀</i>	<i>References</i>
Cholesteryl Bromide Mon.	C ₂ ²	2		10.7	7.45 β = 132°	21.4	1933, 40a.
Cholesteryl Chloride Mon.	C ₂ ²	2		10.3	7.0 β = 131°	21.2	1933, 40a.
Cholesteryl Salicylate C ₃₄ H ₅₀ O ₃ Tri.	C ₁ ¹	1		9.68	12.52	6.31	1934, 334.
Ergosterol C ₂₇ H ₄₄ OH Mon.	C ₂ ²	4	A	α = 85°53', β = 77°41', γ = 84°1'	7.4	39.1	1932, 39.
Lumisterol C ₂₇ H ₄₄ OH Mon.	C ₂ ²	4	A	20.3	β = 65°	20.4	1932, 39.
Calciferol C ₂₇ H ₄₄ OH Mon.	C ₂ ²	8	A	20.8	β = 60°	38.5	1932, 39.
Calciferol Pyrocalciferol (1:1) Mon.	C ₂ ²	4		20.2	7.35 β = 68°	40.0	1932, 39.
Pregandioli Ort.				10.2	7.3	24.6	1932, 38.
α-Dihydroergosterol, Ethyl Alcoholate C ₂₇ H ₄₅ OH, C ₂ H ₅ OH Mon.	C ₂ ²	12	A	30.8	7.4	43.1	1932, 39.
Ketohydroxyoestrin Mon.	C ₂ ²	4	A	7.5	β = 53°	9.06	1932, 37, 38.
α-Follicular Hormone (unstable rhombic form) C ₁₈ H ₂₆ O ₂ Ort.		4		7.84	β = 112°	18.2	1934, 343.
α-Follicular Hormone (stable rhombic form) C ₁₈ H ₂₆ O ₂ Ort.		4		12.0	16.2	7.45	1934, 343.
α-Follicular Hormone Monohydrate C ₁₈ H ₂₄ O ₃ Mon.		4		22.85	7.55 β = 70½°	9.15	1934, 343.
Trihydroxyoestrin Mon.	C ₂ ²	4	A	7.50	22.8 β = 112°	9.06	1932, 37.

(Lactone 135) $C_{23}H_{36}O_2$	Mon.	C_2^2	2	10.6	7.7 $\beta = 79^\circ$	11.7	1934, 18.
Dianhydrodigitoxigenin $C_{22}H_{35}O_2(OH)$	Mon.	C_2^2	2	9.62	7.85 $\beta = 86\frac{1}{2}^\circ$	12.8	1934, 18.
Digitoxigenin $C_{23}H_{37}O_2(OH)_2$	Ort.	V^4	4	18.13	7.16	14.95	1934, 18.
Gitoxigenin $C_{23}H_{37}O_2(OH)_3$	Mon.	C_2^2	8	6.16	13.3 $\beta = 82^\circ$	53.3	1934, 18.
Digitoxigenin $C_{23}H_{37}O_2(OH)_3$	Ort.	V^4	4	9.62	16.75	12.85	1934, 18.
Vitamin B ₄ Hydrochloride $C_{17}H_{18}O_2N_4S_2 \cdot 2HCl$ (Windaus)	Mon.	C_{2h}^6	4	12.62	20.53 $\beta = 66^\circ 5'$	6.96	1933, 39.
Adenine Hydrochloride*	Mon.	C_{2h}^4 or C_2^2		8.71	4.80 $\beta = 62^\circ 0'$	20.00	1933, 39.
Insulin †	Mon.		26	130	100 $\beta = ca\ 90^\circ$	80	1932, 105.
Pepsin	Hex.			67		151	1934, 17.

* The unit cell as stated above contains 4 hydrochloride and 2 H_2O molecules. Crystals of a supposed vitamin B₄ have an almost identical cell; it is concluded therefore that the B₄ is only an impurity in this adenine hydrochloride.

† From the published data it is certain that this cell cannot be the true unit.

Appendix

Bibliography of Crystal Structure Data

This bibliography continues that published as an appendix to the second edition of "The Structure of Crystals." In adding items through 1930, papers by authors who already appear have been given existing numbers with an added a, b, etc.; articles by new authors have been arranged alphabetically with new numbers. The same procedure has been followed in numbering very recent additions to the lists for subsequent years.

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